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DIVISION OF CHEMICAL SCIENCE

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TABLE OF CONTENTS

	Page	Russ. page
General and Inorganic Chemistry		
1. Adsorption of Gas Mixtures. Communication 4. Adsorption of Water and Ethyl Chloride Vapors on Active Charcoal. B. P. Bering and V. V. Serpinsky	851	957
2. Isomerism of the Dibromodinitroplatinate(II) Ion. A. A. Grinberg, A. I. Dobroborskaya, and G. A. Shagisultanova	861	968
3. Electronic Processes in Chemisorption. Communication 2. F. F. Volkenshtein	865	972
4. Solubility of the Elements in Chromium. I. I. Kornilov	871	980
Organic and Biological Chemistry		
5. Splitting of Hydrogen Chloride from $\alpha,\alpha;\alpha,\omega$-Tetrachloroalkanes and α,α,α-Trichloroalkanes. A. N. Nesmeyanov and L. I. Zakharkin	879	988
6. 2-Aminovinyl Ketones. Communication 1. Synthesis of Alkyl 2-Dialkylaminovinyl Ketones. N. K. Kochetkov	883	991
7. Condensation of Meso-halo Derivatives of 1,3-Dioxo Compounds with Urea. L. Sekeresh and G. Fodor	887	996
8. High-temperature Catalytic Dehydrogenation of Ethylcyclohexane. Communication 1. Main Direction of the Reaction. N. I. Shuikin and I. I. Levitsky	895	1003
9. High-temperature Catalytic Dehydrogenation of Ethylcyclohexane. Communication 2. Thermodynamic Equilibrium in the Dehydrogenation of Ethylbenzene under the Conditions of its Formation from Ethylcyclohexane. I. I. Levitsky and N. I. Shuikin	903	1012
10. Reaction of the Grignard Reagent from 3-Chloro-2,4-dimethyl-1-pentene with 2,4-Dimethyl-3-Pentanone, Ethyl Formate, and Amyl Butyrate. V. A. Ponomarenko and T. Ya. Tolkacheva	907	1017
11. Semicatalytic Hydrogenation and Dehydrational Condensation in the Mechanism of the Iso Synthesis. Ya. T. Eidus	913	1024
12. Hydrogen Exchange Between Saturated Hydrocarbons and Sulfuric Acid. D. N. Kursanov, V. N. Setkina, and O. D. Sterligov	921	1035
13. Transformations of Vinyl Ethers. Synthesis of Halo Acetals from Vinyl Ethers. M. F. Shostakovsky and N. A. Gershtein	927	1043
14. Chemical Reactions of Unsaturated and Macromolecular Compounds. Communication 1. Copolymerization of Methacrylic Acid and Alkyl Vinyl Ethers. M. F. Shostakovsky and A. M. Khomutov	931	1048
15. Ionic Polymerization of Vinyl Ethers. M. F. Shostakovsky, B. I. Mikhantyev, and N. N. Ovchinnikova	939	1056
16. Derivatives of Tertiary Unsaturated Alcohols. Communication 1. Synthesis of Acetylenic Acetals from Vinyl Ethers and Acetylenic Alcohols. M. F. Shostakovsky and I. A. Shikhiev	943	1061
17. Cyanine Dyes. Communication 4. Synthesis of 3-Methyl-4-p-tolybenzo[f]quinolinium Iodide, and Some of Its Reactions. G. T. Pilyugin	949	1068
18. Synthesis of Steroid Compounds and Related Substances. Communication XXI. Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene with α,β-Unsaturated Cyclic Ketones. Synthesis of Steroid Ketones Derived from Hydrogenated Cyclopenta[a]phenanthrene and Chrysene. I. N. Nazarov, L. I. Shmonina, and I. V. Torgov	955	1074

(Continued on inside back cover)

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ADSORPTION OF GAS MIXTURES

COMMUNICATION 4. ADSORPTION OF WATER AND ETHYL CHLORIDE VAPORS ON ACTIVE CHARCOAL

B. P. Bering and V. V. Serpinsky

INTRODUCTION

Investigation of the simultaneous adsorption of the vapors of water and of an organic substance on active charcoal presents considerable interest in connection with the unusual character of the adsorption isotherms for water vapor on this adsorbent. As is well known, it has been established as the result of numerous investigations on the adsorption of water vapor on charcoal, carbon black, and graphite that for all these chemically similar adsorbents the adsorption isotherms of water vapor differ greatly in form from those of organic vapors. These facts clearly point to an essential difference in the mechanism of adsorption in the two cases. There is reason to suppose that investigation of the simultaneous adsorption of aqueous and organic vapors on charcoal will enable certain supplementary information to be obtained which is necessary for the elucidation of the nature of the adsorption of water on adsorbents of the active-charcoal type.

These considerations prompted us to make a study of the simultaneous adsorption of water and an organic substance on active charcoal, and for the second component of the gas phase we chose ethyl chloride. In the study of this system we found that it was not possible to make use of the method of measuring adsorption from gas mixtures that we developed and used for the investigation of simultaneous adsorption from the mixtures $CO_2 + C_2H_4$ and $C_2H_4 + C_3H_6$ onto active charcoal [1-3]: it was found that the readings of the gas analyzer were unstable in an atmosphere of ethyl chloride. We, therefore, had to develop a new method of measurement. This new method of measuring simultaneous adsorption from binary gas mixtures, which we have called the "volumetric-gravimetric" method [4], enabled us to carry out the projected investigations. In view of its simplicity and fairly high degree of universality, we shall examine this method in greater detail.

Volumetric-Gravimetric Method

In principle, the volumetric-gravimetric method of measuring simultaneous adsorption from gas or vapor mixtures is as follows. Known amounts of the two components of the gas phase, measured with the aid of gas buret and manometer, are introduced into a vessel of known volume containing the adsorbent, which has been weighed on an adsorption balance. By measuring the total adsorption with the help of the balance and the equilibrium pressure of the gas phase with a manometer, we may determine the adsorption of each component separately and its partial pressure in the gas phase.

Thus, let G be the weight of adsorbent determined on a quartz balance suspended in the vessel, which is of volume V. Let m be the total adsorption of the two components, P the equilibrium pressure of the gas phase, and n_1^0 and n_2^0 the amounts (in moles) of the two components introduced into the vessel; then, treating the gas phase as ideal, we may write the following obvious relationships:

$$m_1 + m_2 = m; \tag{1}$$

$$m_1/M_1 + m_2/M_2 = n_1^0 + n_2^0 - PV/RT = n, \tag{2}$$

(m_1 and m_2 are the values of the adsorption for the two substances [in grams]; M_1 and M_2 are the molecular weights of the components; and n is the total number of moles of the two substances in the adsorption phase).

These equations may be solved for m_1 and m_2 to give the adsorption values for the two components:

$$m_1 = \frac{n - m/M_2}{\frac{1}{M_1} - \frac{1}{M_2}}; \quad m_2 = \frac{n - m/M_1}{\frac{1}{M_2} - \frac{1}{M_1}}. \tag{3}$$

from which we can readily determine the numbers of moles of the two components in the adsorption phase $n_1 = m_1/M_1$ and $n_2 = m_2/M_2$; the corresponding adsorption values for the two components (per gram of adsorbent),

$a_1 = n_1/G$ and $a_2 = n_2/G$; and the number of moles in the gas phase, $n'_1 = n_1^0 - n_1$ and $n'_2 = n_2^0 - n_2$, and so the partial pressures p_1 and p_2 of the two components:

$$p_1 = \frac{n'_1}{n'_1 + n'_2} p; \quad p_2 = \frac{n'_2}{n'_1 + n'_2} p. \tag{4}$$

EXPERIMENTAL

A diagram of the apparatus for measuring the adsorption of the mixture by the volumetric-gravimetric method is given in Figure 1. The sample of active charcoal (G = 0.175 g) was placed in the pan A of the quartz sorption balance B, which was suspended from a hook on an internal dry joint J in the vessel C. The balance was mounted on a glass frame provided with a scale for the readings, which could be made with a constant absolute accuracy over a wide range of spring extension [5]. The position of the pointer could be read within ± 2 divisions of the ocular micrometer of a cathetometer, which corresponds to an absolute displacement of the pointer of ± 0.004 mm. The balance was previously calibrated at the working temperature (74°) of the thermostat in which it was used: it had a sensitivity of 8.58×10^{-6} g per division of the ocular micrometer.

The glass piston pump H was incorporated in the apparatus in order to circulate the gas mixture through the vessel containing the balance and so accelerate attainment of adsorption equilibrium. The gas buret G, which was connected to the manometer M_2, served for the measurement of portions of the two components of the gas mixture. Through the mercury cut-off S_2, which was provided with two ground glass valves, the buret could be connected to one of two reservoirs (not shown in the diagram), containing water and ethyl chloride respectively. Measurements of the pressure of the vapor in the buret and of the equilibrium pressure in the vessel C were performed with two identical manometers M_2 and M_1, the readings being accurate within ± 0.05 mm. A detailed description of the pump H and the manometers has been given in one of our papers [1].

In order to increase the accuracy of pressure measurements on water vapor, it was decided to carry out all measurements at an elevated temperature. For this purpose the adsorbent was placed during the experiment in the thermostat T_1, which was fed through a coil with water from an ultrathermostat. With the help of this thermostat the temperature of the adsorbent was maintained at 74 ± 0.01°. The whole apparatus was placed in the air thermostat T_2 (shown in Figure 1 by the broken line), in which a somewhat lower temperature (72 ± 0.5°) was maintained in order to prevent the possible condensation of mercury vapor on the adsorbent.

Before the simultaneous-adsorption measurements were carried out, preliminary experiments were performed on ethyl chloride alone and on water vapor alone, in order to check the calibration of the balance and of the volume V. The adsorption values calculated from the volumetric measurements were in good agreement with those obtained by direct measurement with the balance. First of all the adsorption isotherms were determined for H_2O and C_2H_5Cl, and then four series of measurements were made on simultaneous adsorption from H_2O / C_2H_5Cl mixtures. Before each series of experiments, the adsorbent was degassed for two hours at 420° to a vacuum of about 1×10^{-4} mm. Hg.

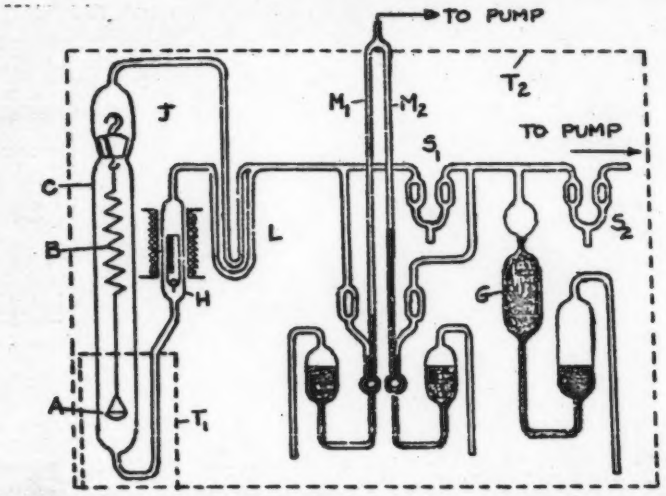

Figure 1. Diagram of apparatus

The substances taken for adsorption were distilled water and a very pure medicinal preparation of ethyl chloride. Both substances were carefully freed from dissolved gases and were contained in reservoirs that were isolated by mercury cut-offs from the remainder of the apparatus.

In the series of experiments on the adsorption of mixtures, a certain amount of C_2H_5Cl was introduced into the buret through the cut-off S_2, S_1 being closed; and after being measured it was transferred quantitatively to the vessel C by cooling the trap L with liquid nitrogen. The change in weight of the adsorbent and the equilibrium pressure were then measured, and after that a portion of water vapor was introduced into the buret. The measured portion of water was transferred through the cut-off S_1 to the vessel C by cooling the trap with liquid nitrogen. In the course of this operation, the greater part of the ethyl chloride adsorbed on the charcoal was desorbed and transferred to the trap. The cut-off S_1 was then closed, the trap L was warmed, the pump H was switched on, and observations were made on the position of the balance and the readings of the manometer M_1. When equilibrium had been established and the equilibrium values of the adsorption and pressure had been measured, the next portion of water was measured in the buret and transferred to the vessel C. In this way, in every series of measurements the total amount of C_2H_5Cl in the gas phase and on the adsorbent remained constant. In this method of measurement, when the trap L warmed up after removal of the Dewar vessel containing liquid nitrogen, first of all the ethyl chloride evaporated and was the first to be adsorbed by the charcoal, and then water evaporated from the trap and the slow process of adsorption of water set in.

Results

With the aid of the method described, measurements were made of the adsorption isotherms of the pure components, H_2O and C_2H_5Cl on active charcoal at 74° over a range of relative pressures p/p_s of 0 to 0.85 (i.e., from 0 to 240 mm Hg) for water and over the range 0 to 500 mm Hg for ethyl chloride; also, four series of adsorption measurements were made on H_2O/C_2H_5Cl mixtures at the same temperature. Since the adsorption of each component of the mixture is a function of two independent variables (the equilibrium partial pressures p_1 and p_2 of the two components), we have

$$a_1 = f_1(p_1, p_2); \quad a_2 = f_2(p_1, p_2). \tag{5}$$

Here, as in the further discussion, the subscript 1 refers to water and the subscript 2 to ethyl chloride.

Figure 2 shows the projection of the experimental points (in coordinates p_2 and p_1) on the coordinate plane $a_i = 0$. The four curves 1, 2, 3, and 4 drawn through these points correspond to the four series of experiments. Each curve refers to a constant amount n_2^0 of ethyl chloride in the system: for curves 1, 2, 3, and 4 the values of n_2^0 are 0.112, 0.552, 1.332, and 3.091 millimoles of C_2H_5Cl respectively.

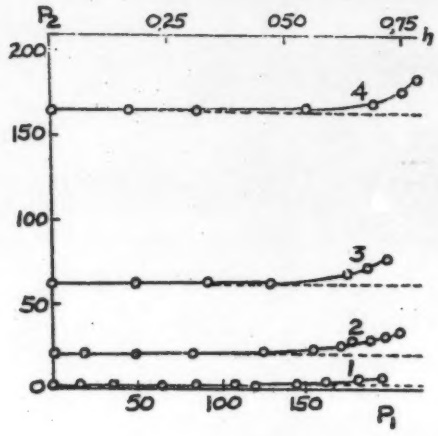

Figure 2. Projection of experimental points on the plane $a_i = 0$.

In Figure 3 the curve A is the adsorption isotherm for water vapor in absence of ethyl chloride, and curves 1–4 represent projections on the coordinate plane $p_2 = 0$ of the water-vapor adsorption isotherms corresponding to curves 1 – 4 in Figure 2. In Figure 4 curves 1–4 are projections on the same coordinate plane $p_2 = 0$ of the C_2H_5Cl adsorption isotherms corresponding to curves 1–4 in Figure 2. In both cases projections of the experimental points are marked by circles.

On the scale chosen the curves in Figures 3 and 4 are practically indistinguishable from those referring not to a constant content of C_2H_5Cl in the system, but to a constant partial pressure p_2 over the adsorbent, i.e., are practically indistinguishable from the curves obtained by taking sections with the planes p_2 = constant of the isothermal adsorption surfaces for H_2O and C_2H_5Cl; these planes are indicated on Figure 2 by the broken lines. On this account we shall consider, for simplicity, that the curves in Figures 3 and 4 correspond to constant values of p_2, equal to 2, 20, 62, and 164 mm Hg for curves 1, 2, 3, and 4, respectively.

Discussion of Results

As will be seen from Figure 3, the presence of ethyl chloride in the gas phase greatly alters the character of the adsorption of water on charcoal. As the partial pressure of C_2H_5Cl increases, the water adsorption isotherms are

displaced in the direction of greater relative pressures h of water vapor, and the slope of the central linear part of the isotherm increases. This observation is in qualitative agreement with the results of Dubinin and Zaverina [6], who studied the effect of the adsorption of benzene and dibutyl phthalate on the form of the adsorption isotherm for water vapor on charcoal and observed a displacement toward the right in the isotherms as the amount of adsorbed benzene increased. The adsorption of ethyl chloride depends in a very peculiar way on the value of the relative pressure of water vapor at constant p_2. The curves in Figure 4 show that as h increases the adsorption of C_2H_5Cl at first remains practically constant, or very slowly falls. At $h > 0.5$, however, there is a sharp fall in the adsorption of ethyl chloride, and for curve 1 the value of a_2 becomes practically zero for $h > 0.7$, i.e., almost the whole of the ethyl chloride is displaced by water under these conditions. The value of h at which displacement of ethyl chloride from the charcoal is almost complete increases as p_2 rises, as will be seen from Figure 4 on passing from curve 1 to curve 4.

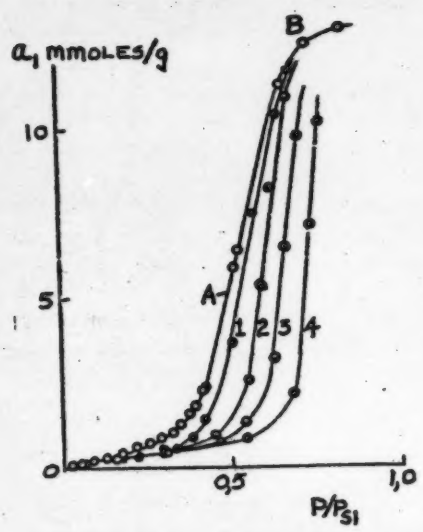

Figure 3. Projection of adsorption isotherm for water on the plane $p_2 = 0$.

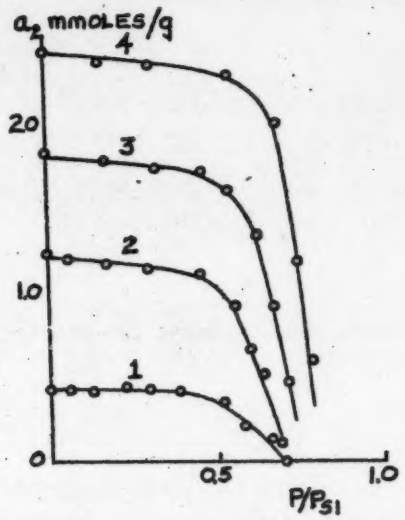

Figure 4. Projection of adsorption isotherm for ethyl chloride on the plane $p_2 = 0$.

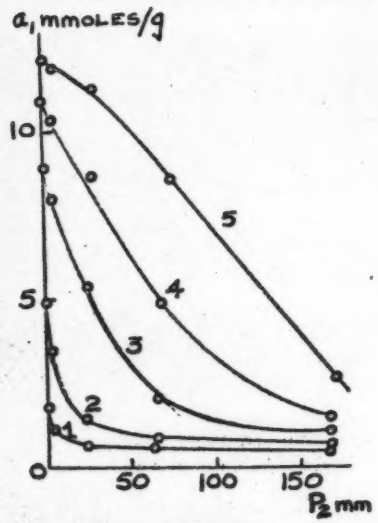

Figure 5. Curves of $a_1 = f_1(p_2)$ for h = const.; 1 – h = 0.40; 2 – h = 0.50; 3 – h = 0.60; 4 – h = 0.65; 5 – h = 0.70

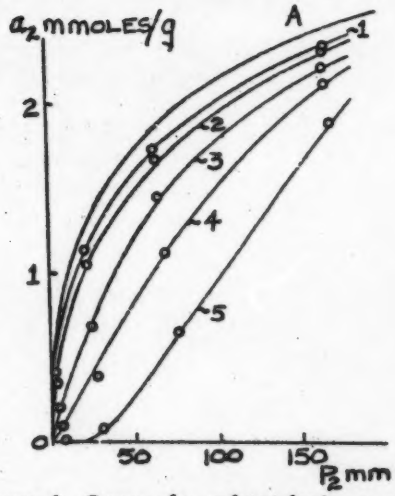

Figure 6. Curves of $a_2 = f_2(p_2)$ for h = const.; A – h = 0; 1 – h = 0.40; 2 – h = 0.50; 3 – h = 0.60; 4 – h = 0.65; 5 – h = 0.70.

In order to obtain a clearer idea of the forms of the surfaces for the adsorption of the two components (Equations 5), we constructed sections of these surfaces made by the planes $\underline{h} = p_2/ps_1 = \text{const}$, using the curves in Figures 2, 3, and 4. The families of curves obtained, $a_1 = \underline{f}_1(C, p_2)$ and $a_2 = \underline{f}_2(C, p_2)$ (the parameter $p_1 = C$) are given in Figures 5 and 6 respectively.

In Figure 5, when $\underline{h} = 0.4$ or 0.5 (curves 1 and 2), there is a marked suppression of adsorption of water to be observed already at comparatively low values of p_2, but as further increase in $\underline{h}$ occurs, the value of p_2 necessary for the displacement of water from the adsorption phase becomes higher and higher. The slope coefficient for curves $\underline{1} - \underline{5}$ at $p_2 = 0$ falls in absolute value in passing from curve 1 to curve 5.

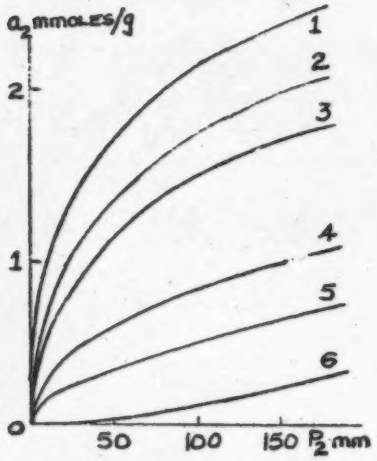

Figure 7. Isotherms $a_2 = \underline{f}(p_2)$ for $a_1 = \text{const}$; $\underline{1} - a_1 = 0$; $\underline{2} - a_1 = 2.0$; $\underline{3} - a_1 = 5.0$; $\underline{4} - a_1 = 8.0$; $\underline{5} - a_1 = 10.0$; $\underline{6} - a_1 = 12.0$.

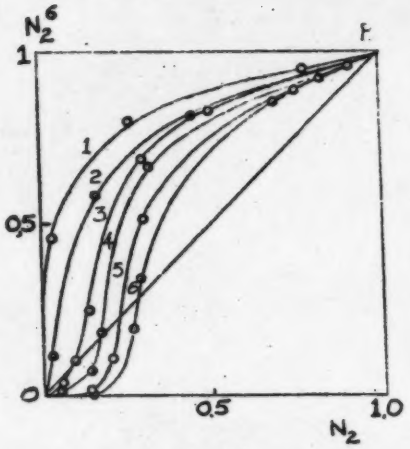

Figure 8. The relation $N_2^{\sigma} = F(N_2)$ for P = const; $\underline{1} - P = 80$; $\underline{2} - P = 140$; $\underline{3} - P = 180$; $\underline{4} - P = 200$; $\underline{5} - P = 220$; $\underline{6} - P = 240$.

It follows from Figure 6 that for values of $\underline{h}$ of up to 0.5 the adsorption isotherms for C_2H_5Cl (curves 1 and 2) do not differ greatly in form from the original adsorption isotherm for ethyl chloride in absence of water (curve A). With further rise in $\underline{h}$ a considerable reduction in the slope of the curve at the origin is to be observed, and at $\underline{h} = 0.7$ (curve 5) the adsorption isotherm changes the sign of its curvature in its initial section and becomes concave.

In order to obtain an idea of the form of the C_2H_5Cl adsorption isotherms for various constant values of water adsorption, we constructed curves of $a_2 = \underline{f}(p_2)$ for $a_1 = \text{const}$, on the basis of the curves in Figures 2 – 4. The curves so obtained are shown in Figure 7, and it will be seen that as a_1 increases the adsorbability of ethyl chloride rapidly falls. The change in the form of the adsorption isotherm is, however, slight, and the rapid change in slope at the beginning of the curve is preserved even at $a_1 = 10.0$ mmoles/ g. This fact leads us to suppose that even when the adsorption of water is high the charcoal surface remains heterogeneous with respect to ethyl chloride. It will be seen that in the interval $a_1 = 10.0\text{-}12.0$ mmoles/ g the C_2H_5Cl adsorption isotherm changes its form and becomes concave. It is only at these values of a_1 that ethyl chloride is practically not adsorbed on charcoal at low pressures (p_2) at the temperature of the experiments. It should be noted that the curve corresponding to $a_1 = 12.0$ is less reliable, since it was constructed by the extrapolation of the curves in Figures 3 and 4.

On the basis of these considerations, we may conclude that the system under examination, $H_2O + C_2H_5Cl$, is considerably more complex than the previously studied systems, $CO_2 + C_2H_4$ and $C_2H_4 + C_3H_6$, and in this connection it should be noted that the rule previously found [2, 3] regarding the linearity of the total-adsorption isosteres is not observed in the system $H_2O + C_2H_5Cl$. Similarly, the relation of the molar fraction N_2^{σ} of ethyl chloride in the adsorption phase to its molar fraction N_2 in the gas phase is considerably more complicated.

Figure 8 shows the relation between N_2^{σ} and N_2 for various values of constant total pressure $\underline{P}$ in the gas phase. For $\underline{P} < 0.5p_{s1}$ the curves of $N_2^{\sigma} = F(N_2)$ are very similar to the corresponding curves for the mixtures studied previously, and the selectivity coefficient α_2 for ethyl chloride varies, for example along curve 1, from 30 to 5. With rise in $\underline{P}$, however, these curves take up an S-shape with a point of inflexion, and their lower sections are below the diagonal OB, along which $\alpha_2 = 1$. The lower parts of these curves (for example, curve 6) up to the point of intersection with the diagonal correspond to values of $\alpha_2 < 1$ (and therefore to values of the selectivity coefficient

for water of $\alpha_1 > 1$), and the parts of the curves lying above this diagonal correspond to values of $\alpha_2 > 1$.

We may conclude from an examination of the curves in Figs. 4 and 5 that the adsorption of a mixture of H_2O and C_2H_5Cl is associated with marked competition between the two types of molecules. As p_1 rises (p_2 being maintained constant), displacement of C_2H_5Cl molecules from the charcoal by water occurs (see Fig. 4), and this process may evidently proceed until the whole of the ethyl chloride is displaced. On the other hand, as p_2 rises at constant p_1 (see Fig. 5), displacement of water molecules from the surface phase occurs, but this process, apparently, cannot lead to the complete displacement of water from the charcoal, at least for values of p_2 below 200 mm Hg.

We shall now make a more detailed examination of the stoichiometry of the displacement, i.e., the question of the ratio in which the molecules of one component may replace those of the other in the adsorption phase. This form of the question has a meaning only when definite conditions are laid down with respect to the values of the partial pressures, for example, the condition that p_1 or p_2 = const. Actually, if we eliminate p_1 or p_2 from Equations 5, we obtain

$$a_1 = \varphi_1(a_2, p_2) \quad \text{or} \quad a_2 = \varphi_2(a_1, p_1). \tag{6}$$

We shall refer to each of the derivatives obtained from Equation 6 as a displacement coefficient γ:

$$\gamma_1 = -\left(\frac{\partial a_1}{\partial a_2}\right)_{p_2=\text{const.}} \quad \text{or} \quad \gamma_2 = -\left(\frac{\partial a_2}{\partial a_1}\right)_{p_1=\text{const.}} \tag{7}$$

In the general case, when we do not know the form of the functions f_1 and f_2, we cannot say anything beforehand about the values of γ_1 and γ_2.

It is not difficult to find expressions for Equations 6 and 7 for the case of the adsorption of a mixture that may be described in the language of Langmuir's theory:

$$a_1 = -\left(1 + \frac{1}{b_2 p_2}\right) a_2 + a_m \quad \text{or} \quad a_2 = -\left(1 + \frac{1}{b_1 p_1}\right) a_1 + a_m \tag{8}$$

and correspondingly

$$\gamma_1 = 1 + \frac{1}{b_2 p_2} \quad \text{or} \quad \gamma_2 = 1 + \frac{1}{b_1 p_1} \; . \tag{9}$$

The coefficients γ_1 and γ_2 therefore depend on p_1 or p_2 and on the adsorption coefficients: as $p_2 \rightarrow \infty$, $\gamma_1 \rightarrow 1$, and as $p_1 \rightarrow \infty$, $\gamma_2 \rightarrow 1$. Hence, in the case under examination, one molecule of the first component displaces one of the second component, only for $p_2 \rightarrow \infty$, i.e., in a saturated monolayer. At lower surface coverage, $\gamma_1 > 1$ and $\gamma_2 > 1$. In the coordinates a_2, a_1, the family of curves described by the first of Equations 8 is a ray of straight lines originating in the point $(0, a_m)$. The slope of these lines falls with rise in p_2 and tends to the value -1 as $p_2 \rightarrow \infty$. The corresponding ray of lines described by the second of Equations 8 originates in the point $(a_m, 0)$, and the slope coefficient of these lines increases with rise in p_1 and tends to the value -1 as $p_1 \rightarrow \infty$.

On constructing the curves $a_1 = \varphi(a_2)$ for the systems studied previously [1-3], we obtained approximately linear curves, and they varied in slope in such a way that the coefficients γ_1 and γ_2 approached the value of unity as p_1 and p_2 increased in value. From the curves in Figs. 5 and 6 we constructed curves showing the dependence of the adsorption of water a_1 on the adsorption of ethyl chloride a_2. The resulting curves for p_1 = const are shown in Fig. 9, and the corresponding curves for p_2 = const are shown in Fig. 10.

As the parameter $h = p_1/p_{s1}$ increases the curve $a_1 = F_1(a_2)$ in Fig. 9 gradually becomes straighter, and its slope increases. The slope of the corresponding curve in Fig. 10 falls with rise in p_2. However, in contrast to the previously examined case of Equations 8 and 9, the limiting value to which the slope coefficient of the linear part of the curve in Fig. 9 tends as p_1 increases is fairly close to -5 (in Figs. 9 and 10 the scale of the abscissa axis is five times as great as that of the ordinate axis). The value to which the slope coefficient of the linear part of the curve in Fig. 10 tends as p_2 increases is also -5 (see the curve corresponding to p_2 = 160). The limiting values of the coefficients γ_1 and γ_2 in the given case are therefore not 1, but 5. In other words, at high pressures five H_2O molecules are needed for the displacement of one C_2H_5Cl molecule.

If we assume that at high pressures p_1 and p_2 corresponding to the limiting value of the γ coefficients we are dealing with spatial displacement from the pores of the charcoal of one liquefied component by another,

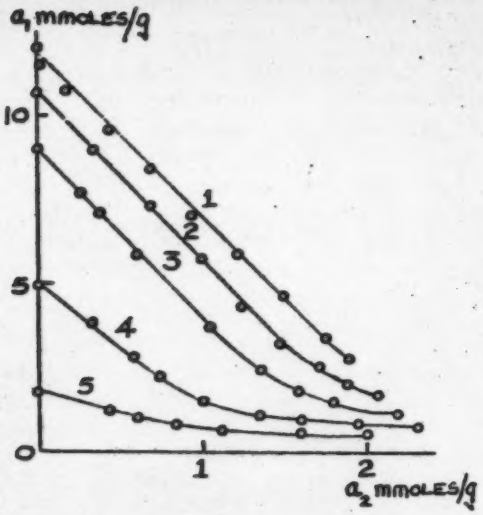

Fig. 9. The relation $a_1 = F_1(a_2)$ (h = const); 1) $h = 0.70$; 2) $h = 0.65$; 3) $h = 0.60$; 4) $h = 0.50$; 5) $h = 0.40$

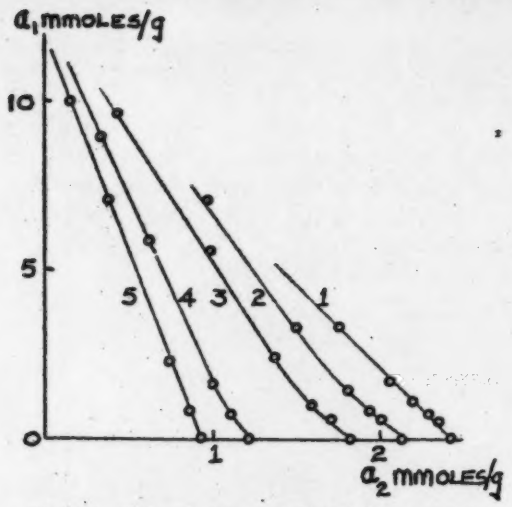

Fig. 10. The relation $a_1 = F_2(a_2)$ (ρ_2 = const); 1) $p_2 = 160$; 2) $p_2 = 100$; 3) $p_2 = 60$; 4) $p_2 = 20$; 5) $p_2 = 10$

also liquefied, component, then the coefficient γ must be equal to the ratio of the molar volumes V_2/V_1 of ethyl chloride and water. Assuming the normal values of the density δ for water and ethyl chloride, we obtain a value of 3.9 for this ratio. It is extremely unlikely that the ratio δ_1/δ_2 in the pores of the charcoal is 1.27 times greater than the corresponding ratio of the normal densities of H_2O and C_2H_5Cl. We therefore consider that the value $\gamma = 5$ contradicts the concept of equivalent-space displacement of one liquid component by another. Moreover, a further argument may be advanced against this concept: the highest relative pressure of ethyl chloride attained in our experiments was 0.033, and at such a low relative pressure, ethyl chloride can definitely not occur in the pores of the charcoal as a liquid phase.

If we assume that water occurs in the adsorption phase as liquid condensed in capillaries, whereas ethyl chloride is adsorbed at the surface of the charcoal, then it is impossible to explain the constancy of γ, since it is obvious that in a system of pores of various dimensions the process of displacement of an adsorbed layer of ethyl chloride by liquid water cannot be characterized by a constant value of γ.

If we regard the sharp rise of the adsorption isotherms for water as the result of capillary condensation, substantial difficulties arise in the explanation of the displacement we have found in curves 1-4 (Fig. 3) in a right-hand direction from the origin, and also of the progressive increase in the steepness of their middle portions. If we apply Thomson's equation to these curves, we shall, of course, obtain a family of various "distribution curves" of pore volume against radius, instead of the single distribution curve that actually characterizes the given porous adsorbent. From the formal point of view, this difficulty can be avoided by ascribing a different value of the contact angle (varying along each curve) to each of the curves in Fig. 3. From our point of view, however, capillary condensation is possible only after the formation of at least a monomolecular adsorbed layer, since the preliminary formation of a meniscus is, of course, bound to occur in this process. If, however, the adsorbent is already covered with a monomolecular layer, it is difficult to imagine that the contact angle can differ from zero.

On account of these considerations, we consider that our results are in conflict with the concept of capillary condensation and that the explanation of the observed phenomena must be based on a different mechanism for the adsorption of water on charcoal, without introduction of the hypothesis of capillary condensation.

It has already been suggested [7] that hydrogen bonds, formed between adsorbed molecules, play an important part in the adsorption of water molecules on the surface of charcoal. It may be supposed that at low surface coverage adsorption is brought about by weak Van der Waals forces between the water molecules and the charcoal surface. As the surface concentration increases, there is an increase in the probability of the formation of complexes consisting of several H_2O molecules united by hydrogen bonds. As is well known, water molecules are not associated in the gas phase, their thermal energy being sufficient to destroy complexes that form. In the surface

layer, however, the field of force of the adsorbent stabilizes the complexes formed. As the presence of water vapor increases little islands of two-dimensional condensed phase appear on the charcoal surface: they are formed of fragmentary chains of water molecules linked together by hydrogen bonds.

Whenever the pressure becomes sufficiently high, this process results in the covering of the whole surface of the charcoal by a network consisting of fragmentary chains of water molecules, so arranged that the dipole moments of the H_2O molecules lie in a plane parallel to the surface of the adsorbent. Such a monomolecular layer of water is not localized and is distinct in principle from the localized monomolecular water layer on an ionic crystal (or silica gel); for the latter case the dipole moments of the water molecules are oriented at an angle to the adsorbent surface and repulsive forces are in operation between the molecules, the formation of hydrogen bonds within the monomolecular layer being impossible. It is in fact the formation of hydrogen bonds between adsorbed molecules that leads to the concavity of the initial part of the adsorption isotherm for water on charcoal (and possibly also in other cases), for negative curvature in the first part of the isotherm is an indication of the predominance of attractive forces between adsorbed molecules [5].

It should be noted that the hydrogen atoms of adsorbed molecules may be regarded, from the point of view that we have developed, as adsorption centers of a peculiar type. It will be readily seen that with increase in surface concentration the number of adsorption centers will not diminish, as in the case of adsorption on an ionic crystal, but increase. It is possible that it is this circumstance that leads to the rapid increase in the steepness of the isotherm for water on charcoal in its middle section.

It should be remembered that the isotherm for the adsorption of water on nonporous carbon black [7] is very similar to that for the adsorption of water on charcoal, a fact that indicates an identical mechanism in both cases.

In our opinion, the rapid increase in the adsorption of water on charcoal in the range of $\underline{h} = 0.4$-0.7 is a change of state in a two-dimensional phase. This two-dimensional condensation process, however, proceeds not at constant pressure p_1, but over a fairly wide range of pressure. The existence of this range may be formally explained by introducing the concept of surface heterogeneity; but there is reason to suppose that the surface of charcoal is very homogeneous with respect to the adsorption of water, since the adsorption potential is determined primarily by the energy of the hydrogen bond, and not by the energy of interaction with the surface. It is possible that even on an ideally homogeneous surface this process of the formation of a condensed two-dimensional phase would take place over a certain range of values of $\underline{h}$.

If we take this mechanism for the adsorption of water on charcoal as a basis, then we must assume that the process leading to the displacement of ethyl chloride by water occurs within a monomolecular layer. It is possible that the equation $\gamma = 5$ is determined by purely energetic considerations. As the heat of adsorption of ethyl chloride on charcoal is about 12 kcal/mole, and the energy of one hydrogen bond in water is about 3.5 kcal/mole, then for $\gamma = 5$ the average number of hydrogen bonds broken per molecule when five H_2O molecules are replaced by one C_2H_5Cl molecule does not exceed $\frac{12}{5 \times 3.5}$, i.e., ≈ 0.75. It may therefore be concluded that the average degree of association of water molecules in the surface layer is greater than two, but probably does not exceed four.

The supposition that the steep rise of the adsorption isotherms for water on charcoal results from a two-dimensional change of state, and not from capillary condensation, permits us to give a qualitative explanation of the displacements in the curves in Fig. 3. It will be evident that the presence of C_2H_5Cl molecules on the surface of the charcoal reduces the probability of the formation of associated complexes $(H_2O)_n$ in the adsorption phase. This results in a displacement of the beginning of the sharp rise in the direction of higher values of $\underline{h}$. Then, as shown above, displacement of C_2H_5Cl molecules occurs, and as a result of this process, the adsorption properties of the surface approximate to those of a surface characterized by isotherm A in Fig. 3. From this point of view, the tendency of the curves in Fig. 3 to come closer together as the adsorption of water increases is a natural one.

We will point out also that, if in accord with the concepts just presented, we consider that point B on isotherm A in Fig. 3 corresponds to a complete monolayer, then, assuming that the area occupied by a water molecule is 10 A^2, we obtain the very reasonable value of ~ 700 sq.m/g for the specific surface of the charcoal. It should however be emphasized that, although the experimental results for the charcoal studied can be explained without introducing concepts concerning capillary condensation, this does not mean, of course, that the process of two-dimensional change of state of water on charcoal may not be complicated in other cases by simultaneously occuring capillary condensation in accord with the concepts of "forced" capillary

condensation developed by Dubinin and Zaverina [8, 9].

The authors have the pleasant duty of expressing their gratitude to M. M. Dubinin and B. V. Ilyin for their constant interest in this work.

SUMMARY

1. A new volumetric-gravimetric method for the measurement of simultaneous adsorption from binary mixtures of gases or vapors on solid adsorbents is described.

2. Measurements have been made of simultaneous adsorption from mixtures of H_2O and C_2H_5Cl on active charcoal at 74° over a range of relative pressure of water vapor of 0-0.85 and over a range of partial pressures p_2 of ethyl chloride of 0-180 mm Hg.

3. The adsorption isotherms for water at constant p_2 are displaced by rise in the value of p_2 to the right from the origin, and the steepness of their linear middle sections increases.

4. Rise in relative pressure h of water vapor to above 0.5 at constant partial pressure of ethyl chloride leads to a sharp fall in the sorption of ethyl chloride. With further rise in h, the ethyl chloride is practically completely displaced from the charcoal by water.

5. An examination has been made of the stoichiometry of adsorptional displacement in the adsorption of binary gas mixtures. It has been shown that on the basis of Langmuir's theory, the displacement coefficient γ should tend to unity as the pressure increases. It has been found that in the adsorption of mixtures of H_2O and C_2H_5Cl on charcoal at high pressures γ approximates to the value 5, so that in adsorptional displacement five H_2O molecules are equivalent to one C_2H_5Cl molecule.

6. The difficulties arising in the interpretation of the results from the point of view of the concept of capillary condensation of water in the given system are pointed out, and one of the other possible mechanisms of adsorption of water on charcoal is examined: it is based on the hypothesis of two-dimensional change of state in the adsorption layer resulting from the formation of hydrogen bonds between adsorbed water molecules.

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ISOMERISM OF THE DIBROMODINITROPLATINATE(II) ION

A. A. Grinberg, A. I. Dobroborskaya, and G. A. Shagisultanova

According to coordination theory, compounds of the type $K_2[PtX_2Y_2]$, in which X and Y are acid residues, should exist in two geometrically isomeric forms of cis and trans structure:

$$\begin{bmatrix} X & & Y \\ & Pt & \\ X & & Y \end{bmatrix} K_2 \text{ (cis)} \qquad \text{and} \qquad \begin{bmatrix} X & & Y \\ & Pt & \\ Y & & X \end{bmatrix} K_2 \text{ (trans)}$$

Many examples are known of similar isomerism in compounds of the type $[Pta_2X_2]$, in which a is an amine and X an acid residue, and also in compounds of the type $[Pta_2a'_2]X_2$, in which a and a' are different amine molecules [1]. However, for compounds in which only the usual acid residues are attached to platinum, such isomerism has not yet been observed. This fact was at one time regarded as an argument in favor of the tetrahedral, rather than the planar, structure for compounds of this type, and it later came to be regarded as a result of the high mobility of coordinated acid residues and the associated tendency to undergo rearrangements.

In 1951 analogous isomerism among quadrivalent platinum compounds was described by Babaeva, who investigated compounds of composition $K_2[Pt(NO_2)_3Cl_3]$ [2].

In the present investigation it has been shown that the compound of composition $K_2[Pt(NO_2)_2Br_2]$ can be obtained in two isomeric forms. It is true that we have not yet succeeded in effecting the complete separation of the isomers and their preparation in the pure state, but the reactions of the salt $K_2[Pt(NO_2)_2Br_2]$ indicate that it is a mixture of two isomers standing in cis-trans relationship to one another.

EXPERIMENTAL

Isomeric forms of the compound $K_2[Pt(NO_2)_2Br_2]$ were obtained by the reaction:

$$K_2[Pt(NO_2)_4] + K_2[PtBr_4] \rightarrow 2K_2[Pt(NO_2)_2Br_2].$$

When equimolecular proportions of $K_2[Pt(NO_2)_4]$ and $K_2[PtBr_4]$ were mixed and heated in a water bath for about thirty minutes, the characteristic color of bromoplatinate(II) slowly disappeared and a golden-yellow solution was obtained, from which, on evaporation, a salt of composition $K_2[Pt(NO_2)_2Br_2]$ separated. When the solution of $K_2[Pt(NO_2)_2Br_2]$, obtained by reaction of $K_2[Pt(NO_2)_4]$ and $K_2[PtBr_4]$ was treated with ammonia, fairly rapid precipitation of a colorless crystalline substance occurred. If this was rapidly filtered off under suction, a second crop of crystals of somewhat different form began to separate after a certain time.

Analysis indicated that both fractions of the salt obtained in this way had a composition corresponding to the formula $[Pt(NH_3)_2(NO_2)_2]$.

Analysis of Fraction I

	Found %: Pt 60.34; 60.34
$[Pt(NH_3)_2(NO_2)_2]$.	Calculated %: Pt 60.78

Analysis of Fraction II

	Found %: Pt 60.71; 60.52; 59.65
$[Pt(NH_3)_2(NO_2)_2]$.	Calculated %: Pt 60.78

It is clear from this that reaction with NH_3 proceeds mainly as follows:

$$K_2[Pt(NO_2)_2Br_2] + 2NH_3 \rightarrow [Pt(NH_3)_2(NO_2)_2] + 2KBr^*$$

The configurations of the salts present in the two fractions were determined by Kurnakov's thiourea reaction. It was found that Fraction I consisted of trans-dinitrodiammineplatinum, and Fraction II of a mixture of cis- and trans-dinitrodiammineplatinums.

In addition, a new reaction was applied for the chacterization of the configurations: it consisted in treatment of the preparation of dinitrodiammineplatinum under test with a few drops of phenolphthalein and a considerable excess (10 moles per mole of salt) of potassium iodide. Trans-dinitrodiammineplatinum gave a yellow precipitate of trans-$[Pt(NH_3)_2I_2]$ (first of all the colorless solution turned yellow).

Analysis of the yellow salt

$[Pt(NH_3)_2I_2]$. Found %: Pt 40.50; 40.54
Calculated %: Pt 40.41

Under the same conditions the cis isomer gave a bright-red solution; evidently, ammonia, labilized by the nitro group situated at the opposite side, was eliminated from the inner sphere.

The fact that the action of ammonia on a solution $K_2[Pt(NO_2)_2Br_2]$ yields not the cis isomer, as would be expected on the basis of Peyrone's rule, but a mixture of both isomers in which the trans form actually predominates, is extremely interesting.

There may be two explanations of this position: 1) it may be supposed that the two isomers are formed by the action of ammonia on one single salt present in the solution, and 2) it may be supposed that two isomers of the salt $K_2[Pt(NO_2)_2Br_2]$, are present in the solution, and these react in different ways with ammonia. The second supposition implies that the salt of composition $K_2[Pt(NO_2)_2Br_2]$ is actually able to exist in cis and trans forms.

In order to decide which supposition is correct, we attempted to effect some separation, if only partial, of the supposed isomers of composition $K_2[Pt(NO_2)_2Br_2]$ by means of fractional crystallization. This operation was carried out as follows: A solution of the salt $K_2[Pt(NO_2)_2Br_2]$, prepared as already described, was evaporated down on a water bath until crystals began to separate, and was then cooled strongly by immersion in ice. The fraction of crystals that separated was filtered off under suction. A further batch of crystals was obtained from the mother liquor by a similar method. The filtered fractions were washed with alcohol and dried at 90-95°.

Fraction I, obtained in this way, was a light-yellow crystalline substance, and Fraction II was somewhat darker in color (with an orange tinge) and turned appreciably darker in the drying process. The two fractions of crystals showed practically no difference in analysis.

Analysis of Fraction I

Found %: ($Pt + K_2SO_4$) 70.65; 70.79; 70.66; 70.68; Pt 37.43; Br 30.28
Calculated %: ($Pt + K_2SO_4$) 70.34; Pt 37.18; Br 30.42

Analysis of Fraction II

Found %: ($Pt + K_2SO_4$) 70.65; 70.60; 70.83; 70.89; Pt 36.87; Br 29.98
Calculated %: ($Pt + K_2SO_4$) 70.34; Pt 37.18; Br 30.42

The analyses show that both fractions are of composition $K_2[Pt(NO_2)_2Br_2]$. We then proceeded as follows: we took equal amounts (0.25 g) of the two fractions and dissolved them in equal amounts of water (2.5 ml). The solutions obtained were somewhat different in color, the solution of Fraction II having an orange tinge.

Ammonia was added to the solutions in the amounts calculated for diammine formation (about 0.1 ml of 18% ammonia solution), and decolorization and precipitation of dinitrodiammineplatinums occurred. Decolorization was considerably slower in the solution of Fraction II.

In both cases two separate fractions of dinitrodiammineplatinum were separated (four batches of salt altogether). Samples from all the batches were analyzed for platinum content, and the results corresponded to the

*At the same time a very small amount of $[Pt(NH_3)_2NO_2Br]$ is formed.

composition $[Pt(NH_3)_2(NO_2)_2]$.

Analysis of Fractions I and II of the ammine from the first fraction of $K_2[Pt(NO_2)_2Br_2]$

$[Pt(NH_3)_2(NO_2)_2]$. Found %: Pt 60.84; 60.19 Calculated %: Pt 60.78

Analysis of Fractions I and II of the ammine from the second fraction of $K_2[Pt(NO_2)_2Br_2]$.

$[Pt(NH_3)_2(NO_2)_2]$. Found %: Pt 60.44; 60.42 Calculated %: Pt 60.78

Tests on all batches were made with the aid of the above-described KI/phenolphthalein reaction, and it was found that the first fractions of $[Pt(NH_3)_2(NO_2)_2]$ obtained from the two fractions of $K_2[Pt(NO_2)_2Br_2]$ gave only a weak pink coloration. The behavior of these fractions in this reaction was not very characteristic. A very distinct difference in behavior in this reaction was shown by the second fractions of the ammines, and the results of these tests were very reproducible. The second fraction obtained from the more difficultly soluble crystals of $K_2[Pt(NO_2)_2Br_2]$ gave a feeble "cis reaction", whereas the corresponding fraction from the readily soluble crystals of $K_2[Pt(NO_2)_2Br_2]$ gave a very intense reaction under the same conditions.

These results show that the salt $K_2[Pt(NO_2)_2Br_2]$ does undergo partial separation into two modifications in the process of fractional crystallization, the more soluble product being enriched in cis isomer. It is evident that both theoretically possible forms are produced in the reaction $K_2[Pt(NO_2)_4]$ with $K_2[PtBr_4]$. This follows directly from Chernyaev's trans-effect principle and the relative closeness of the values of the trans effects of the two acid residues. These forms are bound to differ in their general physical properties and, in particular, their solubilities. Their separation may be complicated by their interconversion, which is possible in principle. Thus, it might be expected that in the process of fractional crystallization the more readily soluble isomer might be transformed into the less soluble form. If the rate of such conversion is sufficiently great, then the more soluble isomer may be largely removed from the solution. Our results show that under our conditions of fractional crystallization a sufficient amount of cis isomer nevertheless remained for it to be detected by the method described.

The action of ammonia on a solution of potassium dibromodinitroplatinate(II) containing both isomeric forms may proceed as follows: cis-Dinitrodiammineplatinum may be formed in the normal way from cis-$K_2[Pt(NO_2)_2Br_2]$ according to the equation:

$$K_2\begin{bmatrix} NO_2 & & Br \\ & Pt & \\ NO_2 & & Br \end{bmatrix} + 2NH_3 \longrightarrow \begin{bmatrix} NO_2 & & NH_3 \\ & Pt & \\ NO_2 & & NH_3 \end{bmatrix} + 2KBr.$$

The trans-dinitrodiammineplatinum may, however be formed in several ways. It may, for example, arise from cis-$K_2[Pt(NO_2)_2Br_2]$ via intermediately formed cis-bromonitrodiammineplatinum, which is converted via potassium trans-bromodinitroammineplatinate(II) into the trans-dinitrodiammine isomer.

trans-Dinitrodiammineplatinum may be formed also via the same intermediate products from potassium trans-dibromodinitroplatinate(II). Equations representing these respective changes are:

$$K_2\begin{bmatrix} NO_2 & & Br \\ & Pt & \\ NO_2 & & Br \end{bmatrix} + 2NH_3 \longrightarrow \begin{bmatrix} NH_3 & & NH_3 \\ & Pt & \\ NO_2 & & Br \end{bmatrix} + KNO_2 + KBr \longrightarrow$$

$$\longrightarrow K\begin{bmatrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & Br \end{bmatrix} + NH_3 + KBr \longrightarrow \begin{bmatrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & NH_3 \end{bmatrix} + 2KBr \qquad (1)$$

$$K_2\begin{bmatrix} NO_2 & & Br \\ & Pt & \\ Br & & NO_2 \end{bmatrix} + 2NH_3 \longrightarrow \begin{bmatrix} NH_3 & & Br \\ & Pt & \\ NH_3 & & NO_2 \end{bmatrix} + KNO_2 + KBr \longrightarrow$$

$$\longrightarrow K\begin{bmatrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & Br \end{bmatrix} + NH_3 + KBr \longrightarrow \begin{bmatrix} NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & NH_3 \end{bmatrix} + 2KBr \qquad (2)$$

SUMMARY

1. It has been shown that, when equimolecular amounts of $K_2[PtBr_4]$ and $K_2[Pt(NO_2)_4]$ react, the product has the composition $K_2[Pt(NO_2)_2Br_2]$, and behaves like a mixture of geometric isomerides.

2. Treatment of a solution of the salt $K_2[Pt(NO_2)_2Br_2]$, obtained as indicated above, with ammonia yields trans-dinitrodiammineplatinum containing cis-dinitrodiammineplatinum impurity.

3. A new reaction has been applied for the distinguishing of the two isomers of dinitrodiammineplatinum.

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ELECTRONIC PROCESSES IN CHEMISORPTION

COMMUNICATION 2•

F. F. Volkenshtein

In the preceding paper [1] we postulated that the adsorbent surface is an ideal plane. Also, we considered that a one-electron bond between an adsorbed atom and the surface is so weak (in comparison with a two-electron bond), that its effect can in general be neglected.

In this paper we shall examine the mechanism of chemisorption without making these two assumptions. The paper, like the preceding one [1], is a condensed (qualitative) exposition of the main results of a series of theoretical investigations carried out by the author.

"Thermal Disorder" on the Surface of a Crystal, and its Role in Adsorption

Let us examine a real surface, which is distinguished from an ideal surface by the presence of defects of various kinds which disturb the strictly periodic structure of the surface. We must here distinguish between macro- and micro defects.

A macro defect is a disturbance over a region having dimensions considerably greater than those of the unit cell of the crystal; for example, fissures in the crystal surface and macroscopic occlusions. We shall not examine such defects here.

A micro defect is a disturbance having dimensions of the same order as those of the unit crystal cell. When there is a micro defect, the periodic structure of the surface is practically re-established at a distance equal to several times the lattice constant. We shall confine ourselves here to a consideration of defects of this sort. In other words, we shall be dealing not with a model of an ideal surface, as in the previous paper [1], but with a somewhat idealized model of a real surface [2, 3].

As examples of micro defects present on all real surfaces we may note the following: a) a vacant lattice point formed by the removal of an ion from the surface layer of the lattice (Fig. 1, a); b) an ion or atom normally found in the lattice, but lying on the surface (rejected from a lattice point, or introduced from outside) (Fig. 1, b); c) a foreign atom or ion lying on the surface (Fig. 1, d); or situated at a lattice point, i.e., replacing an ion proper to the lattice (Fig. 1, c).

The presence of defects is a characteristic of what may be termed "disorder" at the surface of the crystal. In disorder as a whole, two components must be distinguished: "biographic" and "thermal" components. "Biographic disorder" is that part of disorder that is preserved at the absolute zero of temperature; it is the irreversible part. The degree of "biographic disorder" is determined by the technology of the sample—the whole of its previous history; it is the disorder acquired by the lattice "from birth", as it were. On this component of disorder there is superposed the reversible "thermal disorder", which increases as the temperature rises. In fact, as the temperature rises, there is an increase in the dissociation of the ions from the lattice points into the intermediate space, and also in their ejection onto the surface of the crystal. On the other hand, as the temperature falls the degree of order in the lattice increases: ions return to their lattice points and the degree of disorder diminishes. The lattice itself can thus both produce and efface defects: this is a fundamental point.

In the electron economy of the lattice defects play a dual part: some of them are electron acceptors, i.e., traps for conductivity electrons; others are electron donors, i.e., the reservoir from which the conductivity zone obtains free electrons. Defects, therefore, play the part of localization centers for free electrons or for free holes.

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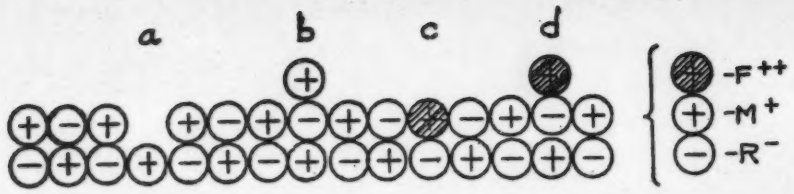

Fig. 1.

In chemical language: they are localization centers for free valencies, which wander over the crystal surface. In other words, such wandering valencies become attached at places where the periodic structure of the lattice is disturbed, and are localized at these places.

Surface defects may therefore be regarded as adsorption centers. Such a concept is in accord with Taylor's views and may be regarded to some extent as an interpretation of them: according to Taylor adsorption centers are formed by geometric heterogeneities on the surface, and on our idealized surface such heterogeneities are represented by micro defects.

Under normal conditions, the concentration of free electrons is negligibly low compared with that of localized electrons, i.e., the electrons held at defects. In other words, the number of freely wandering (non-localized) valencies is low compared with the number of valencies localized at defects. Under these conditions adsorption on free electrons may be neglected in comparison with adsorption on defects. Adsorption on defects (one- and two-electron bond) has been examined by Bonch-Bruevich [4].

It must be noted that the presence of defects on the surface does not imply energetic heterogeneity of the surface, which is associated with the presence of adsorption centers of various kinds. If, in fact, the adsorption centers are defects of only one particular kind, all characterized by the same heat of adsorption q, then our surface is energetically homogeneous from the adsorption point of view.

The adsorption properties of such a surface have been investigated in detail. Adsorption isotherms for such a surface have been found to have a Freundlich form (the index having the value of 1/2). The differential heat of adsorption is a function of the surface coverage, and the adsorption kinetics are also typically non-Langmuir. In other words, such a surface, which is homogeneous in the usual sense of the word (adsorption centers of only one kind!), behaves as a heterogeneous surface.

The cause of this behavior is that the number of adsorption centers on our surface does not remain constant, but changes with temperature. In other words, the specific non-Langmuir properties of the surface are determined by the thermal component of the disorder. If thermal disorder is neglected, only biographic disorder being retained, then all formulas are automatically transformed into the usual formulas of Langmuir theory. Actually, adsorption centers, treated as micro defects of the surface or, more exactly, as electrons (or free valencies) localized at these defects, participate not only in adsorption and desorption reactions, but also, of course, in the reactions of production and effacement of centers by the lattice itself. These reactions proceed on the surface along with the adsorption and desorption reactions.

Consideration of these reactions implies consideration of thermal disorder, and ignoring them implies a return into the framework of Langmuir theory, which relates to a constant number (independent of temperature) of adsorption centers, i.e., ignores thermal disorder in comparison with disorder of biographic origin.

"Weak" and "Strong" Bonds in Chemisorption

We shall now return to the picture of the ideal surface. As we have seen [1], two types of bond are possible between a univalent electropositive atom A and the adsorbent surface.

1. There is the one-electron (comparatively weak) bond produced by the drawing of a valency electron of atom A out of the atom on to the lattice. With respect to a free electron of the lattice, which travels in the surface conductivity zone, the atom A adsorbed in this way constitutes a "trap", i.e., acts as a foreign acceptor, and may be represented in the energetic spectrum of the crystal as a local acceptor level (Fig. 2, a).

2. If the adsorbed atom A, bound to the surface by this one-electron bond, captures a free electron of the lattice, the one-electron bond passes, as has been shown, into a str ..ger, two-electron bond.

The "strengthening" of the bond may be regarded as the saturation of the valency of atom A resulting from the acquiring of the free electron from the lattice. This "strengthening" of the bond is represented on Fig. 2, a by the appearance of an electron in the local level of A. Electronic processes at the surface of the crystal may thus be described in the language of the energy scheme for the foreign semiconductor, which is represented in Fig. 2, a.

In the preceding paper we neglected the "weak" (one-electron) bond in comparison with the "strong" (two-electron) bond. We shall now examine the more general case. We shall consider that the chemically adsorbed atom may have a "weak" or a "strong" bond with the surface [5].

Transitions are possible between these states. These transitions are regulated by the "electron-hole" gas on the crystal surface. Let us turn to Fig. 2, b. The curves represent diagrammatically the energy W of the system as a function of the distance r of the atom A from the surface. The different curves correspond to different electronic states of the system. Curve aa is the adsorption curve on the unactivated crystal, i.e., on a crystal that contains no free electrons and holes. Curve bb is curve aa displaced upward and parallel to itself. It corresponds to adsorption on an activated crystal containing a free electron (in the surface conductivity zone) and a corresponding free hole (in the normal surface zone).

Curves aa and bb correspond to "weak" (one-electron) adsorption. Curve cc corresponds to adsorption by a "strong", two-electron bond. The transition from curve bb or aa to curve cc is associated with the "strengthening" of the bond between the atom A and the surface. These transitions are shown respectively by the arrows 1 and 2 on Figures 2, a and b. The reverse transitions (1' and 2') represent "weakening" of the bond.

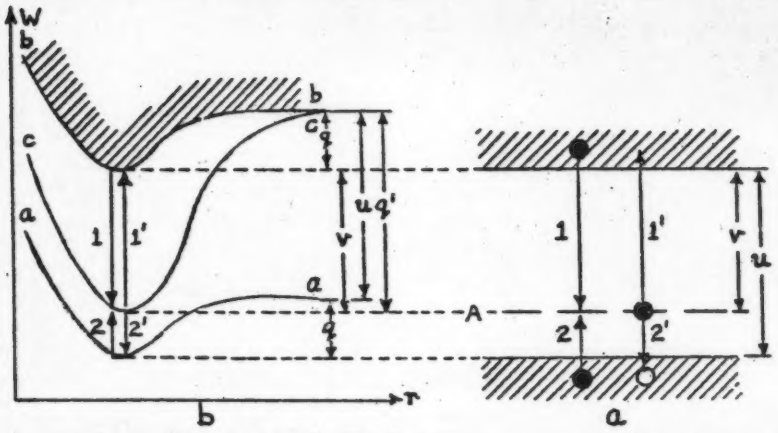

Fig. 2.

The "strengthening" of a bond is therefore accompanied by the disappearance of a free electron from the conductivity zone (transition 1) or the formation of a free hole in the normal zone (transition 2). "Weakening" of a bond, on the contrary, is characterized by the appearance of an electron in the conductivity zone (transition 1') or the filling of a hole in the normal zone (transition 2'). Bond "strengthening" and "weakening" result from electron exchange with the surface.

At equilibrium, a definite fraction of the adsorbed atoms are in the state of "strong" adsorption, and the remainder are in the state of "weak" combination with the surface. Let N be the total number of adsorbed atoms, and N' the number of atoms in the state of "strong" adsorption. We shall refer to the quantity

$$\eta = \frac{N'}{N} \qquad (1)$$

as "degree of combination"; it represents the fraction of the total number of adsorbed atoms that are "strongly" adsorbed, or, in other words, the probability that a given adsorbed atom will have a "strong" linkage with the surface. At the same time η characterizes the relative mean life of the atom in the "strongly" adsorbed state.

The value of η is determined by the concentration of electron gas at the surface of the crystal; we shall denote this concentration by $\underline{n}$, and $\underline{v}$ will be the "affinity energy" of the adsorbed atom A for a free electron of the lattice (Fig. 2, $\underline{a}$). The relation between η and $\underline{n}$ is given by the formula:

$$\eta = \frac{1}{1 + \frac{c}{n} e^{-\frac{v}{kT}}}. \qquad (2)$$

The greater, therefore, the concentration of electron gas (at the given temperature), the greater the fraction of adsorbed atoms that is to be found in the "strongly" adsorbed state (we are at present considering electropositive univalent A atoms).

On the other hand, the concentration of electron gas, other things being equal, depends on the coverage of the surface with adsorbed atoms, and η is therefore a function of the coverage. For not too small coverages we have:

$$\eta = \sqrt{\frac{c'}{N}} e^{-\frac{u-v}{kT}} \qquad (3)$$

We see that the "degree of combination" of a given atom becomes less as new atoms take their places on the surface. Every adsorbed atom "feels", as it were, the presence on the surface of all the remaining atoms, even though there is no direct interaction between the adsorbed atoms (we ignore it in the calculation). We are dealing here with a special type of interaction resulting from electron exchange with the surface, an interaction that is transmitted by the electron gas.

The presence of two types of bond between the adsorbed atom and the surface and the possibility for an adsorbed atom to pass from one type of linkage to the other are reflected in the laws of adsorption. At low coverage, at which, from the point of view of Langmuir's theory, Henry's law must hold, we obtain a Freundlich isotherm (with an index of 1/2); the kinetics of adsorption are also non-Langmuir. In particular, the coverage of the surface by "strongly" adsorbed atoms follows Benham's law:

$$N' = Ae^{-\frac{u-v}{2kT}} \sqrt{pt}, \qquad (4)$$

and, as will be seen, the dependence on temperature is typical for so-called activated adsorption, the activation energy being

$$\epsilon = \frac{1}{2}(u-v)$$

Our homogeneous surface therefore behaves in a certain sense as a heterogeneous one. We are concerned here with heterogeneity of a special type. Our surface actually contains adsorption centers of only one particular type (M^+ ions of the surface layer serve as centers of this sort). Each adsorption center may, however, be bound to any given adsorbed atom by one of two different types of bonds, and in the course of the life of the atom in the adsorbed state the character of its linkage with the given adsorption center may vary.

The departures from the Langmuir laws may be treated as a manifestation of this peculiar type of heterogeneity. On the other hand, these departures may be treated as the result of the special type of interaction between the adsorbed atoms which we have already discussed, namely, interaction effected by means of the electron gas at the surface of the crystal. The concepts of "interaction" and "heterogeneous surface", therefore, in a certain sense merge together. In other words, when electron exchange reactions are taken into account, the distinction between these concepts becomes blurred: this peculiar kind of heterogeneity and this peculiar kind of interaction present themselves as two aspects of one and the same thing—electron exchange processes.

If we ignore these processes, i.e., put $\overline{\eta} = 0$, our formulas are automatically converted into the corresponding Langmuir formulas. The surface becomes a purely Langmuir surface. These processes, however, cannot be

ignored, for electron exchange reactions have heats of reaction of the same order of magnitude as those for adsorption (the energies u, v, and q in Fig. 2 have values of the order of tenths of an electron-volt).

Reactivity of Chemically Adsorbed Atoms

The presence of bonds of two types between adsorbed atoms and the surface is of great importance in catalysis. A given atom differs in reactivity according to the state, "strong" or "weak", of its linkage with the surface. In the first case its valency is saturated, and in the second case its valency remains unsaturated. We shall suppose (this is the simplest supposition) that an atom is reactive only while its valency is unsaturated. Atoms, therefore, that are "strongly" bound to the surface do not participate in reaction.

The reactivity of an adsorbed atom may be characterized by the quantity

$$1-\eta = \frac{N-N'}{N} \qquad (5)$$

This quantity is the probability that an adsorbed atom will be found in the reactive condition, and at the same time it indicates the fraction of the total number of adsorbed atoms that may participate in reaction, i.e., may be found in a "weak" state of linkage to the surface. It will be seen (from Equation 2) that the reactivity is the lower, the higher the concentration of the electron gas on the crystal surface (other conditions being equal).

Up to now we have considered a univalent electropositive atom, but these considerations can be applied also to any radical having one positive valency. They may be applied also the case of a univalent electronegative atom, or a radical having one negative valency; in this case, however, the word "electron" must be replaced everwhere by the word "hole". Hence, the reactivity of an adsorbed electronegative atom is the lower, the higher the concentration not of the electron gas, but of the "hole" gas on the crystal surface (other conditions being equal).

It should be noted that in the case of thermal equilibrium the product of the concentrations of the electron gas and of the "hole" gas is always a constant for a given crystal at a given temperature. Hence, the factors leading to the enrichment of the electron gas lead to impoverishment of the "hole" gas, and conversely. The introduction of foreign matter (acceptor or donor) into the crystal constitutes such a factor.

Factors that intensify the reactivity of electropositive atoms (radicals) suppress the reactivity of electronegative atoms (radicals).

As we have already noted, a free electron on the surface of the crystal may be treated as an unsaturated positive valency. Analogously, a free hole may be treated as a negative valency. Under normal conditions, hence, there are a certain number of free positive and negative valencies on the crystal surface. The concentrations of these valencies are respectively equal to those of the electron and hole gases.

The number of such valencies changes with changing conditions (for example, increases with rise of temperature) and may be artificially increased or reduced as the result of external action on the crystal. This behavior is characteristic for the surface of an ionic crystal. Another characteristic feature is that not every free valency is localized: it may wander freely on the surface.

If there are defects on the surface (of "thermal" or "biographic" disorder), then, as we have seen, wandering valencies may be trapped (localized) at these defects, and, on the other hand, valencies localized at defects may escape, i.e., become delocalized. When a wandering free valency meets the unsaturated valency of an adsorbed atom (or radical), mutual valency saturation occurs, this being accompanied by localization of the wandering valency and the transition of the adsorbed atom (radical) into a state of "strong" linkage with the surface (i.e., to the loss of its reactivity).

Up to now we have considered atoms or radicals that have unsaturated valencies in the free state. Such atoms or radicals may appear on the surface in the course of the adsorption of a saturated molecule, i.e., a molecule having no free valencies, when the adsorption of such a molecule is accompanied by its dissociation, as often occurs.

Let us examine a molecule AB formed form two atoms, or groups of atoms, A and B linked together by a single bond (Fig. 3, a). When such a molecule is adsorbed, the bond linking these two groups of atoms in the molecule may be disrupted by a free electron (or, in other cases, by a free hole) of the crystal lattice. In other words, an encounter with a free electron (or with a free hole) may lead to the dissociation of the molecule. One

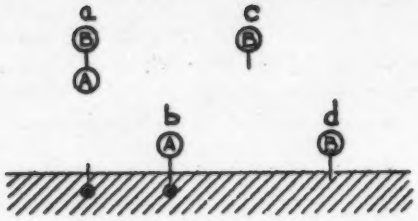

Fig. 3.

of the dissociation products, the radical A for example, is then found to be adsorbed and attached to the surface by a "strong" bond formed with the participation of the free electron or hole that caused the dissociation and captured the radical A (Fig. 3, b). The other dissociation product, the radical B for example, preserves its unsaturated valency and passes into the gas phase (Fig. 3, c), or is adsorbed on the surface, attaching itself by a "weak" bond (Fig. 3, d). The net result is that there appear on the surface the adsorbed radicals A and B in the state of "strong" and "weak" linkage and capable of transition from one state to the other, a state that may be described as the localization and delocalization of an electron or hole, i.e., of a positive or negative valency belonging to the crystal surface.

Reactions occurring on the crystal surface may therefore be regulated by an electron or hole gas. Some stages of reaction may be speeded up and others may be slowed down, depending on the rise in the concentration of the electron gas or the diminution in that of the hole gas. From this there arises a possible mechanism for the action of foreign matter on the activity of a catalyst [6, 7, 8]. The introduction of foreign matter, in fact, changes the concentrations of the electron and hole gases, and as a result the contamination must affect the reactivity of adsorbed atoms (radicals). It should be noted that adsorbed atoms themselves, and molecules participating in reaction or appearing as products of reaction, act as foreign substances on the crystal surface (i.e., affect, as we have seen, the concentration of the electron and hole gases). Reactions occurring on the surface, therefore, may retard themselves (autopoisoning) or accelerate themselves (autopromotion). It should be noted also that this electronic mechanism for the action of foreign material does not require that direct contact should occur between reacting atoms on the one hand, and foreign atoms on the other. The effect of foreign matter is transmitted over a distance. Here we again meet a peculiar type of interaction effected by means of an electron or hole gas.

SUMMARY

1. Theoretical calculations, the results of which have been given here briefly in qualitative fashion, have been made with the object of discovering the elementary (micro-scale) mechanism of a phenomenon. Being concerned with a micro mechanism, these calculations are in their essence quantum-mechanical calculations, and it is this circumstance that determines the most characteristic features of the theory developed. One such characteristic feature is that the theory must operate with simplified and schematized models: with models that lend themselves to quantum-mechanical calculation. The fundamental features of the mechanism then become manifest in their clearest and least obscured form.

2. Another characteristic feature is that, while attempting to explain experimentally observed regularities and to discover the possible source of these regularities, the theory leads us to completely new ideas and concepts which did not figure previously in theories of adsorption. This is again the result of the quantum-mechanical approach to the problem.

3. Finally, for the theory of chemisorption, developed from this aspect, as has been done here, it is characteristic that its basis is the modern theory of solids and that it utilizes the concepts and apparatus of the modern theory of solids. The entry of the theory of solids into the adsorption and catalysis field, i.e., into the territory of physical chemistry, is necessary and inevitable for the creation of a micro-scale theory of chemisorption. The theory of chemisorption, of course, is still not a theory of catalysis, but it forms the first step in the direction of the creation of a theory of catalysis: its ideas and concepts form the foundation on which a theory of catalysis may be built.

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SOLUBILITY OF THE ELEMENTS IN CHROMIUM

I. I. Kornilov

The metal chromium is an element of Group VI of Mendeleev's periodic system of elements, its closest analogs being molybdenum and tungsten. Owing to their high melting points, great strength, and good chemical stability, chromium and its analogs are of considerable interest for the preparation of alloys of practical importance. Chromium, molybdenum, and tungsten alloys, as also the now widely used alloys having an iron, nickel, or other base, are capable of wide application in a number of branches of our technology.

Chromium, like many other metals, by interaction with other metals, or in some cases metalloids, is able to form solid solutions and metallic compounds. The character of the chemical interaction between different metals is determined experimentally by the construction and study of the phase diagrams of the metal systems. We have already published a review of investigations (up to 1953) on the phase diagrams of chromium systems [1].

The crystallographic regularities that are observed now permit us to examine questions relating to the solubility of elements in metals from a general point of view. The circumstances determining the ability of metals to form solid solutions are as follows [2]: 1) closeness in the chemical properties of the elements, which is to be related to their positions in the periodic system; 2) small differences in interatomic distances, i.e., 8-10% for unlimited solid solutions (i.e., formed in all proportions) and 14-16% for limited solid solutions; 3) isomorphism of the crystal lattices of the metals (for formation of unlimited solid solutions).

By applying these conditions we may predict the possibility of the formation of solid solutions between the metals, including chromium. On the basis of the examples afforded by our study of the solubility of the elements in iron [3] and nickel [4, 5], we have demonstrated the existence of the appropriate functional relationship to the factors cited above in the case of the formation of iron and nickel solid solutions. A similar type of relationship in the formation of solid solutions has been observed previously for aluminum [6], copper [7], magnesium [8], and other metals.

Let us examine the solubility of the elements in chromium, following the periods and groups of Mendeleev's periodic system. Table 1 contains information on the differences in atomic diameter between these elements and chromium, and, in the cases where experimental data are available, the solubilities of the elements in chromium are given (at the final temperature of the crystallization).

Data relating to the distribution of elements in the periodic system—which determine the differences and similarities in the chemical properties of the atoms and in their crystal structure—permit us to reach definite conclusions concerning the solubility of the elements in chromium. The elements of Periods I and II—H, Li, Be, B, C, N, and O—are, with the exception of beryllium, characterized by relatively great differences in atomic diameter (from that of chromium) (Table 1). Accordingly, even if hydrogen, with its small atomic diameter, should be found to give solid solutions of insignificant concentration with chromium, then they will only be of an intrusion type. Hydrogen absorbed under the conditions of the electrolytic method for preparing chromium is almost completely removed in a subsequent high-temperature treatment in high vacuum. One of the methods of refining electrolytic chromium is based on this circumstance [10].

This indicates the weakness of the bond between hydrogen atoms and chromium in the solid state and the absence of stable solid solutions of hydrogen in chromium. Lithium, which has a high atomic diameter, greatly different (21.8%) from that of chromium, and which occupies a place far removed from that of chromium in the periodic system, not only does not form solid solutions with chromium, but, in general, does not react with it either in the liquid (molten), or in the solid state. Lithium forms neither solid solutions nor compounds with chromium. The absence of chemical reaction with chromium is characteristic for all the analogs of the lithium, the alkali metals of Group I (Na, K, Rb, and Cs). They, like lithium, neither mix with chromium in the liquid state not give solid solutions with it.

TABLE 1

Solubility of the Elements of the Periodic System in Chromium

Period	Element	Atomic diameter (A)	Atomic diameter difference from that of Cr (%)	Solubility at final temperature of crystallization wt-%	Solubility at final temperature of crystallization atom-%	Supposed solubility
1	2	3	4	5	6	7
I	H	1.2	53.2	Unknown		Insoluble
II	Li	3.13	21.8	Unknown		Insoluble
	Be	2.25	12.4	–	9.3	–
	B	1.94	24.5	Unknown		Very limited solubility
	C	1.54	40.0	Unknown		B > C
	N	1.42	44.7	Unknown		C > N
	O	1.32	48.6	Unknown		N > O
III	Na	3.83	49.0	Unknown		Insoluble
	Mg	3.20	24.5	Unknown		Insoluble
	Al	2.80	8.9	29.0	44.11	–
	Si	2.34	8.9	10.0	17.07	–
	P	2.20	14.4	Unknown		Limited solubility
	S'	2.0	22.2	Unknown		Very limited solubility
IV	K	4.76	85.2	Unknown		Insoluble
	Ca	3.93	53.0	Unknown		Insoluble
	Se	3.32	29.2	Unknown		Insoluble
	Ti	2.93	14.0	Unknown		–
	V	2.69	4.7	Unknown		–
	Cr	2.57	–			–
	Mn	2.60	1.2	60	58.68	–
	Fe	2.54	1.2	Unlimited		–
	Co	2.50	2.7	41.0	38.01	–
	Ni	2.49	3.1	35	32.80	–
	Cu	2.55	0.8	Insoluble		–
	Zn	2.748	6.9	Unknown		Insoluble
	Ga	2.74	6.6	Unknown		Insoluble
	Cl	2.78	8.2	Unknown		Insoluble
V	As	2.80	8.9	Unknown		Insoluble
	Rb	5.4	110.0	Unknown		Insoluble
	Sr	4.29	67.0	Unknown		Insoluble
	V	3.62	40.8	Unknown		Insoluble
	Zr	3.19	24.2	Unknown		Very limited solubility
	Nb	2.94	14.4	Limited		–
	Mo	2.80	8.9	Unlimited		–
	Te	–	–	–		–
	Ru	2.66	3.5	Unknown		Limited solubility
	Rh	2.667	4.4	Unknown		Limited solubility
	Pd	2.745	6.8	10	5.14	–
	Ag	2.883	12.2	Does not mix		–
	Cd	3.042	18.4	Does not mix		–
	Zn	3.138	22.0	Unknown		Insoluble
	Sn	3.168	23.2	Does not mix		Insoluble
	Sb	3.228	25.6	12	5.5	–
VI	Cs	5.40	110	Unknown		Insoluble
	Ba	4.48	74.4	Unknown		Insoluble
	La	3.64	41.7	Unknown		Insoluble
	Hf	3.17	23.4	Unknown		Very limited solubility
	Ta	2.94	14.4	Limited		–
	W	2.82	9.7	Unlimited		–

TABLE 1 (continuation)

1	2	3	4	5	6	7
	Re	2.75	7.0	Unknown		Limited solubility
	Os	2.70	5.1	Unknown		Limited solubility
	Ir	2.709	5.4	Unknown		Limited solubility
	Pt	1.769	7.8	—		Limited solubility
	Au	2.877	11.9	10		—
	Hg	3.10	20.4	Does not mix		—
	Tl	3.427	33.4	Unknown		Insoluble
	Pb	3.494	36.0	Does not mix		—
	Bi	3.64	41.7	Does not mix		—
VII	Ra	—	—	—		—
	Th	3.60	40.0	Unknown		Insoluble
	U	2.81	9.3	Unknown		Limited solbuility

In the case of beryllium, more favorable conditions exist for the formation of solid solutions with chromium. The difference in atomic diameter between beryllium and chromium is only 12.4%, and this circumstance favors the dissolution of beryllium in chromium. According to recent data from the literature [9], beryllium will alloy with chromium and forms solid solutions of high concentration.

The remaining elements of Period II—B, C, N, and O—show an ever increasing difference in diameter (from that of chromium). As will be seen from Table 1, the atomic diameters diminish from boron to oxygen. Accordingly, the solubility of these elements in chromium, if they have any, will fall progressively in this series of elements. Although there are no data in the literature in this case, we must nevertheless suppose that these elements fall into the following order with respect to solubility: B > C > N > O.

The sharp fall in the ability of chromium to form solid solutions with carbon, nitrogen, and oxygen explains the highly deleterious effect of these elements on the properties of chromium. When they are present in an insignificant concentration in chromium, the chromium carbides, nitrides, and oxides formed in hundredths or thousandths of one percent greatly impair the mechanical properties of the chromium, and increase its hardness and brittleness [10]. The deleterious effects of hydrogen, carbon, nitrogen, and oxygen on the properties of chromium are convincingly demonstrated in the papers [10] and [11]. It may be considered, therefore, on the basis of atomic diameter relationships, that only beryllium and boron are able to yield solid solutions with chromium, beryllium being able to dissolve in chromium to the extent of 9%, and boron, possibly, to the extent of tenths or hundredths of one percent.

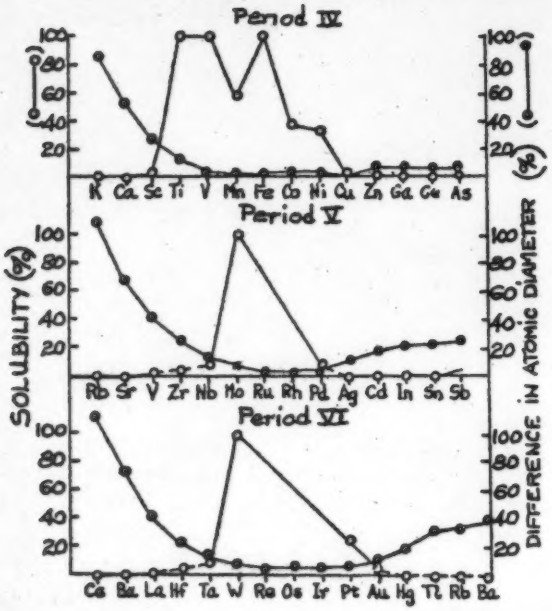
Elements of Period III, Na, Mg, Al, Si, P, and S, depending on their positions in Mendeleev's system of elements and on the differences of their properties from those of chromium, behave differently. Sodium and magnesium, the elements furthest removed from chromium and having atomic diameter differences of 49.0% and 24.5%, respectively, do not interact with chromium: they form neither liquid nor solid solutions with it. Other elements analogous to magnesium behave similarly toward chromium. Also calcium, strontium, and barium — the remaining elements of the alkaline earth group — do not interact with chromium. The higher affinity of metals of this group for oxygen and halogens, as compared to the affinity of chromium, and their complete insolubility in chromium in the molten or solid state make it possible to apply some of the alkaline earth metals, e.g. magnesium and calcium, in a displacement reaction that leads to the preparation of pure chromium. This is the basis of the method of preparing very pure chromium by the reduction of chromic chloride with metallic calcium or magnesium [11].

Of the elements following in this period, aluminum and silicon have diameters that are closer to that of chromium, the differences being 8.9% in each case. Both elements accordingly have appreciable solubility in chromium (Table 1). The formation of unlimited solid solutions between chromium and silicon is excluded, in spite of the favorable diameter relation, because of the differences in the atomic and crystalline structures of chromium and the metalloid silicon. Aluminum and silicon, which form limited solid solutions with chromium, are of value for the improvement of the properties of metallic chromium: they find application as components of chromium alloys [12]. The two succeeding elements, phosphorus and sulfur, which differ from chromium appreciably (14.4% and 20%) in atomic diameter, should not yield solid solutions of appreciable concentration with chromium. Although there are no data in the literature on the solubility of phosphorus and sulfur in chromium in the solid state, it may be asserted that the solubility of phosphorus, if determined, will be not more than some tenths of one percent, while that of sulfur, of course, will be still less. Phosphorus and sulfur, being elements of low solubility in

chromium, have a deleterious effect on the properties of metallic chromium. This effect of sulfur and phosphorus on chromium is analogous to the similar deleterious effect of these elements on the properties of iron and nickel.

The atomic diameter differences with respect to chromium, and the solubilities in chromium, are shown for the elements of the long periods IV, V, and VI in the figure below. An examination of the relationships between these curves permits us to make interesting inferences concerning the dependence of the chrome-solubility of the elements on their positions in these periods. We shall examine the elements of the even and odd rows of these periods separately. As stated above, all the alkali and alkaline earth metals of these periods fail to interact with chromium and do not form either liquid or solid solutions with it.

On the basis of atomic diameter relationships, it may be supposed that chromium will also fail to give solid solutions with scandium, yttrium, and lanthanum. As we pass, however, to the metals of Groups IV, V, VI, VII, and VIII of the even rows of these periods, the atomic diameters become closer to that of chromium, thus favoring formation of chromium alloys with these metals. For example, the elements of Period IV, Ti, V, Mn, Fe, Co, and Ni, are in the same row as chromium. They differ little from chromium in atomic diameter, and they form solid solutions with chromium. Titanium, in the high-temperature modification that is isomorphous with chromium (space-centered lattice), forms unlimited solid solutions with chromium at high temperatures [13], even though there is a difference in atomic diameter of 14% under room temperature conditions. This may be explained as follows. As we have shown [14], owing to their differing coefficients of expansion, the relations between the atomic diameters of metals change at high temperatures. In the case of chromium and titanium, for which α has the values 8.1×10^{-6} and 7.2×10^{-6} cm respectively, it may be supposed that, owing to the differing coefficients of expansion, the difference in atomic diameter will be reduced. This is the explanation of the unlimited solid solutions formed by chromium and the high-temperature β-modification of titanium [13].


Period IV
K Ca Sc Ti V Mn Fe Co Ni Cu Zn Ga Ge As
Period V
Rb Sr V Zr Nb Mo Ru Rh Pd Ag Cd In Sn Sb
Period VI
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Rb Ba
SOLUBILITY (%)
DIFFERENCE IN ATOMIC DIAMETER (%)
100
80
60
40
20

On the basis of the above-stated rules for the formation of unlimited solid solutions, it may be asserted that chromium must form unlimited solid solutions with vanadium and iron (α-modification), since these have similar atomic diameters and isomorphous crystal structure. There are no exact data in the literature on vanadium, but it is known that at high temperatures chromium gives unlimited solid solutions with α-Fe. The possibility indicated by the similarity in atomic diameters of the formation of unlimited solid solutions of chromium with manganese, cobalt, and nickel is not realized owing to their nonisomorphous crystalline structures and the existence of various modifications of manganese and cobalt. For this reason these three metals form only limited solid solutions with chromium (Table 1 and figure).

The elements of the remaining two even rows (6 and 8) of these periods behave analogously to the elements of the fourth row with respect to chromium. This analogy is readily revealed by comparing the solubilities in chromium of the metals of corresponding groups, taking into account the differences in atomic diameter. Thus, the metals of Group IV, i.e., the titanium analogs zirconium, hafnium, and thorium, show, unlike titanium, a growing difference in atomic diameters (24.2, 23.4, and 40.0 respectively). This is bound to lead to the inability of these metals to form solid solutions with chromium. Although there are no data in the literature regarding the solubilities of zirconium, hafnium, and thorium in chromium, it must be supposed that these solubilities are either insignificant (Zr and Hf), or absolutely zero (Th).

From the atomic diameter relationship we may predict also the existence of only limited solid solutions in chromium of the Group V metals niobium and tantalum. Having a difference in atomic diameter of only 4.7%, V and Cr, as stated above, can form unlimited solid solutions, but the vanadium analogs niobium and tantalum, which differ in atomic diameter from chromium by 14.4%, can form only limited solid solutions. A different position is found for the chromium analogs molybdenum and tungsten. They occur in the chromium group and have differences in atomic diameter of 8.9% and 9.7% respectively. On the basis of these data we suggested already in 1948, when examining multicomponent solid solutions of iron with chromium, molybdenum, and other metals [15], that it was possible for molybdenum and tungsten to form unlimited solid solutions with chromium. This suggestion was made in spite of the data then existing in the literature [16] concerning the formation of eutectic mixtures of chromium with molybdenum and tungsten. In experimental investigations that appeared at that time our suppositions received confirmation [17]. The question of the formation of unlimited solid solutions of chromium with molybdenum and tungsten has now been unequivocally solved. Owing to the somewhat greater difference in atomic diameter between chromium and tungsten that exists at low (room) temperature, the unlimited solid solutions formed by these metals are stable only at high temperatures, at which, of course, we may form an idea of the reduction in this difference from the relation between the coefficients of linear expansion [14]. It has been established experimentally that, on being cooled, the unlimited solid solutions of chromium in tungsten separate into two solid solutions. There is no information in the literature relating to the solubility of uranium in chromium. On the basis of the small difference in atomic diameter (9.6%) and the occurrence of the metals in the same group, it may be predicted that they will be found to form limited solid solutions. Formation of unlimited solid solutions is excluded in this system because of the nonisomorphous structure of uranium and its various modifications.

TABLE 2
Binary Chromium Systems

No.	System	No.	System	No.	System
	Unlimited solid solutions	4	Cr–Si	17	Cr–Ir; Cr–Pt
1	Cr–Ti (β)	5	Cr–Mn	18	Cr–Au
2	Cr–V	6	Cr–Co	19	Cr–U and others. Two
3	Cr–Fe (α)	7	Cr–Ni	20	immiscible layers: sys-
4	Cr–Mo	8	Cr–Zr		tems containing metals
5	Cr–W	9	Cr–Nb		of the alkali and alkaline
	Limited solid solutions	10	Cr–Ru		earth groups (with the ex-
1	Cr–Be	11	Cr–Rh		ception of beryllium and
2	Cr–B	12	Cr–Pd		some elements of Subgroup
3	Cr–Al	13	Cr–Hf		B (Pb, Bi))
		14	Cr–Ta		
		15	Cr–Re		
		16	Cr–Os		

As regards the remaining elements of the even rows of the long periods—Ru, Rh, Pd; Os, Ir, Pt—in spite of the closeness in atomic diameter, they cannot give unlimited solid solutions with chromium owing to their nonisomorphous crystal structures. They will all form only limited solid solutions with chromium. The data in the literature relating to the interaction of palladium and platinum with chromium [18, 19] confirm the possibility of forming only limited solid solutions with these metals. With regard to the other elements (Ru, Rh; Os, Ir), although there are no data in the literature, limited solubility in chromium may again be predicted.

As regards the solubilities of elements of the odd rows of Periods IV, V, and VI (or Subgroup B of the periodic system), it must be stated that, like their solubilities in iron and nickel [2, 3], these do not only conform to the rules derived for the solubilities of elements of a given subgroup, particularly metals of Subgroup A. The data in

the literature enable us to state that the elements Cu, Zn, Ga; Ag, Cd; In, Au, Hg, Tl, Pl, Bi and Po, in accordance with their positions in the period system (the most far removed from chromium) are, with the exception of gold, unable to give solid solutions with chromium. Many of them do not mix with chromium even in the liquid state (Pb, Bi, and others), but form two layers. The chromium-gold system gives mutually limited solutions, yielding a phase diagram of the peritectic type.

The elements that are nearer to chromium (Ge, As, Sn, Sb) are able to interact with it and form limited solid solutions and compounds having bonds of the metallic type. There are indications in the literature [16] that Sn and Sb have limited solubility in chromium. The existence of limited solid solutions may be postulated for Ge and As, as analogs of Sn and Sb having even lower atomic diameter differences from chromium.

After an examination, therefore, of the solubilities of the great majority of the elements in chromium, we may present a classification of chromium solid solutions as binary systems. In Table 2 data are given on binary metal systems containing chromium, which are classified as unlimited solid solutions, limited solid solutions , and systems in which two immiscible layers are formed.

As will be seen from Table 2, there are only five binary systems containing chromium that form unlimited solid solutions, and four of these have been studied experimentally; more than twenty systems form limited solid solutions, and most of these have not been studied.

SUMMARY

1. An examination of the solubilities of elements in chromium reveals regularities that are analogous to those that characterize the solubility of elements in other metals, such as iron, nickel, and copper.

2. The formation or nonformation of solid solutions of elements in chromium is determined by the relative similarity or dissimilarity of the chemical properties of the elements, as revealed by Mendeleev's periodic law.

3. On the basis of these concepts it is possible to predict the ability or inability of the elements of the periodic system to form solid solutions with chromium.

4. It is possible either to confirm the conclusions derived from crystallographic laws for the formation of metallic solid solutions by reference to information available in the literature on the solubility of one or other element in chromium or, on the other hand, to predict the ability or inability of chromium to form solid solutions in systems not yet studied experimentally.

5. It may be asserted that chromium forms unlimited solid solutions with titanium (in its high-temperature β-modification), vanadium, molybdenum, and tungsten, but only limited solid solutions with beryllium, boron, zirconium, hafnium, uranium, rhenium, and all metals of Group VIII (the iron and platinum group) with the exception of α-Fe, which has a structure isomorphous with that of chromium; with the last, chromium forms unlimited solid solutions.

6. Neither the metals furthest removed from chromium—the alkali and alkaline earth metals of Groups I and II (with the exception of beryllium)—nor those which are most different from chromium with respect to atomic diameter can form solutions with chromium, either in the solid or in the liquid state.

7. Examination of the solubility of elements of the periodic system in chromium in binary systems permits us to extend these conclusions in order to predict the ability or inability for chromium to form more complex solid solutions in ternary, quaternary, and more complicated systems.

8. Data on the solubility of elements in chromium in binary, ternary, and more complicated systems permit us to determine the possibility of preparing chromium alloys of simple or complex composition, corresponding to regions of unlimited or limited solid solutions of chromium.

9. The regularities established with respect to the solubility of the elements in chromium permit us to examine the question of the formation of solid solutions based on chromium analogs—molybdenum and tungsten. Certain regularities that have been demonstrated for chromium should be found valid also for the solubility of elements of the periodic system in molybdenum and tungsten.

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SPLITTING OF HYDROGEN CHLORIDE FROM

α,α,α,ω-TETRACHLOROALKANES AND α,α,α-TRICHLOROALKANES

A. N. Nesmeyanov and L. I. Zakharkin

Halogen derivatives of hydrocarbons of the types $Cl(CH_2CH_2)_nCCl_3$ and $H(CH_2CH_2)_nCCl_3$ have become readily accessible by the telomerization reaction of ethylene with carbon tetrachloride and chloroform respectively [1]. Comparatively little study has been devoted to the reactivities of these compounds. Among the possible changes that they may undergo, an important place must be assigned to reactions involving removal of the elements of hydrogen chloride as a means of passing to unsaturated polyhalo derivatives. By the removal of the elements of hydrogen chloride from 1,1,1,3-tetrachlorpropane with alcoholic alkali, two substances have been obtained, 3,3,3-trichloropropene and 1,1,3-trichloropropene, which were readily separated by distillation [2].

The removal of elements of hydrogen chloride from higher tetrachloroalkanes containing trichloromethyl groups has been described only in patents [3]. It is there indicated that the splitting off of hydrogen chloride catalytically and by alkaline agents involves only the chlorine of the trichloromethyl group, giving trichloroalkenes of the structure $CCl_2 = CH-(CH_2CH_2)_nCH_2Cl$. We have found that, when the reaction is effected with alcoholic alkali, it does not proceed in one direction only: we obtained a mixture of products having close boiling points that were difficult to separate. It should be noted that constants given in the patents for the compounds obtained by removal of hydrogen chloride, e.g. 1,1,5-trichloropentene, have been found to be inaccurate, as is evident from the great discrepancy between the found and calculated values of molecular refraction. We considered that it would be of great interest to apply catalytic methods for the removal of elements of hydrogen chloride from these polyhalo derivatives. There are a number of examples in the literature of removal of hydrogen chloride from polyhalo derivatives in presence of aluminum chloride; thus, we have the preparation of hexachloropropene from heptachloropropane [4], the preparation of tetrachloroethylene from pentachloroethane [5], and other examples [6]. In all these cases the reaction was carried out at a comparatively high temperature, which limited the field of application of the method. Cases are known of the removal of hydrogen chloride by heating with anhydrous ferric chloride, for example, that of DDT [7], which was also carried out at a comparatively high temperature.

We have found that hydrogen chloride is readily split from α,α,α,ω-tetrachloroalkanes and α,α,α-trichloroalkanes in presence of small amounts of aluminum chloride or, particularly, anhydrous ferric chloride. Reaction begins at room temperature, and for its completion a short time at 40-60° is required; dichlorovinyl derivatives, $ClCH_2(CH_2CH_2)_nCH = CCl_2$ and $CH_3(CH_2CH_2)_nCH = CCl_2$ are obtained in good yield. Under these conditions no by-products are formed and isomerization of the paraffin chain does not occur. The reaction is general for polyhalo derivatives of the structures indicated: we have by this method removed elements of hydrogen chloride from 1,1,1,5-tetrachloropentane, 1,1,1,7-tetrachloroheptane, 1,1,1,9-tetrachlorononane, 1,1,1-trichloropropane, 1,1,1-trichloropentane, and 1,1,1-trichloroheptane.

EXPERIMENTAL

1,1,5-Trichloropentene

a) 1,1,1,5-Tetrachloropentane (210 g) was heated with anhydrous ferric chloride (3 g) at 45-55° for 2 hours 30 minutes. During this time 32.6 g of hydrogen chloride was evolved. The reaction mixture was poured into water in order to dissolve the ferric chloride. The product obtained was then washed with a 10% solution of caustic soda and dried over calcium chloride. Vacuum fractionation through a 40-cm column yielded 151 g (87%) of trichloropentene and 24 g of unchanged tetrachloropentane.

b) Tetrachloropentane (42 g) and aluminum chloride (0.5 g) were heated together at 35-45° for 40 minutes; 7 g of hydrogen chloride was evolved. Aluminum chloride was removed by careful washing with water and then 10% caustic soda, and the product was dried over calcium chloride. Vacuum fractionation yielded 26 g (77%) of trichloropentene and 4.2 g of unchanged tetrachloropentane. The 1,1,5-trichloropentene had b.p. 68-69°/7 mm, n_D^{20} 1.4892; d_4^{20} 1.2724; found MR 39.37; calculated MR 39.42. The literature [3] gives n_D^{25} 1.4878; d_4^{25} 1.2893, found MR 38.76.

	Found %:	C 34.42; 34.45; H 4.07; 4.10
$C_5H_7Cl_3$.	Calculated %:	C 34.57; H 4.03

Hydrolysis of the trichloropentene with concentrated sulfuric acid gave a 92% yield of 5-chlorovaleric acid. From this, via the acid chloride, the amide of 5-chlorovaleric acid, m.p. 78-79°, was prepared. In admixture with authentic amide it melted at 78-79°. The trichloropentene obtained therefore contained a normal chain.

1,1,7-Trichloroheptene

A mixture of 108 g of tetrachloroheptane and 2 g of anhydrous ferric chloride was heated for three hours at 45-55°; 15.2 g of hydrogen chloride was evolved. Vacuum fractionation yielded 76.1 g (73%) of trichloroheptene and 8 g of unchanged tetrachloroheptane. 1,1,7-Trichloroheptene had b.p. 66-67°/ 1 mm or 101-102°/ 8mm; n_D^{20} 1.4850; d_4^{20} 1.1902; found MR 48.52; calculated MR 48.66. The literature [3] gives n_D^{25} 1.4850.

	Found %:	C 41.52; 41.58; H 5.40; 5.56
$C_7H_{11}Cl_3$.	Calculated %:	C 41.68; H 5.45

1,1,9-Trichlorononene

Tetrachlorononane (50 g) and anhydrous ferric chloride (1.5 g) at 45-55° for three hours yielded 31.6 g (73%) of trichlorononene and 8 g of unchanged tetrachlorononane. 1,1,9-trichlorononene had b.p. 91-92°/ 1.5 mm, n_D^{20} 1.4834; d_4^{20} 1.1342; found MR 57.83; calculated MR 57.90.

Hydrolysis of the trichlorononene yielded 9-chlorononanoic acid, from which, via the acid chloride, the amide, m.p. 76-77°, was prepared. In admixture with authentic amide it melted at 76-77°. The trichlorononene therefore contained a normal carbon chain.

1,1-Dichloropropene

1,1-Dichloropropene was prepared in 85% yield; b.p. 77-78°; n_D^{20} 1.4450; d_4^{20} 1.1687.

1,1-Dichloropentene

From 74 g of trichloropentane and 1.5 g of anhydrous ferric chloride at 40-50° for three hours, 46.2 g (81%) of dichloropentene and 5.1 g of unchanged trichloropentane were obtained. 1,1-Dichloropentene had b.p. 127-128°; n_D^{20} 1.4548; d_4^{20} 1.0899; found MR 34.59; calculated MR 34.55.

	Found %:	C 43.17; 42.98; H 5.93; 5.86.
$C_5H_8Cl_2$.	Calculated %:	C 43.16; H 5.75

Hydrolysis of the dichloropentene with concentrated sulfuric acid yielded valeric acid, from which, via the acid chloride, the anilide, m.p. 62.5-63°, was prepared. In admixture with authentic valeranilide, it melted at 62.5-63°.

1,1-Dichloroheptene

1,1-Dichloroheptene was prepared from trichloroheptane and anhydrous ferric chloride in 80% yield. 1,1-Dichloroheptene had b.p. 68-69°/14 mm; n_D^{20} 1.4589; d_4^{20} 1.0430; found MR 43.76; calculated MR 43.79.

	Found %:	C 50.05; 50.04; H 7.26; 7.22
$C_7H_{12}Cl_2$.	Calculated %:	C 50.29; H 7.18.

Hydrolysis of the dichloroheptene with concentrated sulfuric acid yielded heptanoic acid, from which the anilide, m.p. 64-65°, was prepared via the acid chloride. The mixed melting point test gave 64-65°.

SUMMARY

1. A method has been proposed for the splitting of hydrogen chloride from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes and α,α,α-trichloroalkanes by heating these substances with catalytic amounts of anhydrous ferric chloride.

2. It has been shown that no isomerization of the carbon chain occurs under the conditions used for the removal of the elements of hydrogen chloride in presence of anhydrous ferric chloride or aluminum chloride.

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2-AMINOVINYL KETONES

COMMUNICATION 1. SYNTHESIS OF ALKYL 2-DIALKYLAMINOVINYL KETONES

N. K. Kochetkov

Alkyl 2-dialkylaminovinyl ketones $RCOCH = CHNR'_2$ belong to a very interesting, but little studied, class of so-called "enamine" compounds. They are among the simplest members of this class, and they exhibit very clearly the characteristic features of the chemical behavior of enamine compounds. 2-Dialkylaminovinyl ketones may be prepared by the reaction of 2-hydroxyvinyl ketones with secondary amines, but this method finds its main application in the preparation of compounds of complex structure [1, 2]. Also, 2-dialkylaminovinyl ketones have been prepared by the addition of amines to ketones containing a triple bond [3, 4]. This method of synthesis can scarcely be regarded as convenient from the preparative point of view owing to the low accessibility of the starting materials. Owing to the fact that the simplest members of this class of compounds are relatively inaccessible, their chemical behavior has not been studied in sufficient detail, in spite of the interest that they undoubtedly present.

Continuing our investigations of the chemical reactions of alkyl 2-chlorovinyl ketones, we have made a detailed study of the reactions of these with amines with the object of developing a convenient synthesis of N-substituted 2-aminovinyl ketones. There are indications in the patent literature [5] that alkyl 2-chlorovinyl ketones react with amines with formation of 2-aminovinyl ketones, and it is recommended that this reaction be performed in an organic solvent. Numerous repeats of the synthesis under various conditions showed that 2-aminovinyl ketones were indeed formed, but in yields not exceeding 15-25%. Further work in this direction enabled us to simplify and greatly improve this reaction. It was found that the reaction of alkyl 2-chlorovinyl ketones proceeds most smoothly in aqueous medium, and this fact made it possible for us to develop a very simple and convenient method for the synthesis of alkyl 2-dialkylaminovinyl ketones in yields of 60-85%. The best results were obtained in the reaction when the 2-chlorovinyl ketone was added gradually to an aqueous solution of the amine, taken in a quantity of rather more than two moles per mole of 2-chlorovinyl ketone; the reaction then went very vigorously and was not accompanied by any appreciable side reactions:

$$RCOCH = CHCl + 2NHR'_2 \rightarrow RCOCH = CHNR'_2 + NHR_2 \cdot HCl.$$

The amine concentration is of considerable importance: it is most convenient to use an aqueous solution of about 50% strength, the yield being appreciably reduced when more dilute solutions are employed.

The method we have developed for the synthesis of N-substituted alkyl 2-aminovinyl ketones makes it possible to obtain considerable quantities of these substances in a very short time and renders them readily available for further study and application. By this method we have obtained several previously unknown alkyl 2-dialkylaminovinyl ketones, and the yield and constants of these are given in the table.

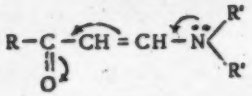
All the compounds prepared are yellowish oily liquids that can be preserved for a long time without change. They are miscible in all proportions with water and with most organic solvents. The physical constants of the substances obtained are given in the table. First of all, the anomalously high boiling points of alkyl 2-dialkylaminovinyl ketones attract attention: they are 60-70° higher than those of their saturated isologs. For example, 4-dimethylamino-2-butanone boils at 57-58°/18 mm; i.e., about 70° below the b.p. of the alkyl 2-dialkylaminovinyl ketone of analogous structure, 4-dimethylamino-3-buten-2-one. All the compounds prepared show also a very high exaltation of molecular refraction (4-5 units).

TABLE

Properties of Alkyl 2-Dialkylaminovinyl Ketones

Formula	Yield (%)	B.p. (°C, p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	EMR
$CH_3COCH = CHN(CH_3)_2$	76.5	101-102 (5)	1.5562	0.9734	37.38	33.40	3.98
$CH_3COCH = CHN(C_2H_5)_2$	83.5	124-125 (6)	1.5378	0.9344	47.26	43.63	4.63
$CH_3COCH = CH$-N(-CH_2-CH_2-)-CH_2	70.0	154-155 (7)	1.5730	1.0103	49.97	45.05	4.92
$n\text{-}C_3H_7COCH = CHN(CH_3)_2$	61.0	120-121 (5)	1.5364	0.9339	47.18	42.63	4.55
$i\text{-}C_4H_9COCH = CHN(CH_3)_2$	66.0	124-125 (4)	1.5270	0.9245	51.61	47.25	4.36

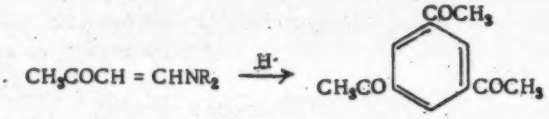
Already on the basis of the physical properties (solubility, high boiling point), we may infer the presence of considerable polarity in alkyl 2-dialkylaminovinyl ketone molecules resulting from interaction between the carbonyl group and the free electron pair on the nitrogen:



This suggestion is well confirmed by results obtained for the dipole moments of these compounds, which have been determined by A. N. Shidlovskaya. Other investigators [4] have come to a similar conclusion on the basis of adsorption spectra studies.

The chemical properties of alkyl 2-dialkylaminovinyl ketones are in accord with this hypothesis. The above scheme, in which the carbonyl group is conjugated with the electron pair of the nitrogen atom, is bound to result in a reduction in basic character and in the suppression of the activities both of the double bond and of the carbonyl group.

Actually, alkyl 2-dialkylaminovinyl ketones have practically no basic properties. Under the action of acids they are rapidly hydrolyzed at the nitrogen-carbon bond. Thus, even a very short treatment with warm acetic acid brings about the decomposition of 4-dimethylamino-3-buten-2-one, a quantitative yield of 1,3,5-triacetylbenzene being obtained; mineral acids react in similar fashion even in the cold:



Alkyl 2-dialkylaminovinyl ketones form picrates, but these are comparatively unstable, and are partially destroyed during recrystallization. The suppression of basic properties and the lability of the C—N bond are manifestations of the operation of a well-known principle of vinylogy. Alkyl 2-dialkylaminovinyl ketones are vinylogs of dialkylamides of acids, and their behavior corresponds to the behavior of amides.

EXPERIMENTAL

I. 4-Dimethylamino-3-buten-2-one

4-Chloro-3-buten-2-one (16.0 g) was added gradually to 70 ml of a 40% aqueous solution of dimethylamine with vigorous stirring and application of cooling in an ice-salt mixture. The reaction was very vigorous and was accompanied by considerable evolution of heat. The homogeneous reaction mixture was stirred for 30 minutes at room temperature, and was then saturated with potassium carbonate and extracted with ether in a liquid extractor for 12 hours. The ether extract was dried over calcined potassium carbonate, the ether was distilled off, and the residue was vacuum-distilled, when it all came over at 131-133°/20 mm, the yield being 13.5 g (76.5%). After redistillation 4-dimethylamino-3 buten-2-one had the following constants:

b.p. 101-102° (5 mm); d_4^{20} 0.9734; n_D^{20} 1.5562; found MR 37.38; calculated for $C_6H_{11}ON$ MR 33.40; EMR 3.98.

	Found %:	N 12.24; 12.40
$C_6H_{11}ON$.	Calculated %:	N 12.37

4-Dimethylamino-3-buten-2-one is a yellowish oil having a feeble odor reminiscent of amides. It may be preserved for a long time without change. It mixes in all proportions with water and organic solvents. It gives a cherry-red color with ferric chloride.

The picrate was prepared in ether; m.p. after careful recrystallization from alcohol: 116-118°.

	Found %:	N 16.47; 16.38
$C_{12}H_{15}O_8N_4$	Calculated %:	N 16.31

II. 4-Diethylamino-3-buten-2-one

4-Diethylamino-3-buten-2-one was prepared in similar manner to the preceding substance from a solution of 85 g of diethylamine in 90 ml of water and 58.0 g of 4-chloro-3-buten-2-one. The yield was 66 0 g (83.5%). After redistillation 4-diethylamino-3-buten-2-one had the following constants: b.p. 124-125° (6 mm); d_4^{20} 0.9344; n_D^{20} 1.5378; found MR 47.26; calculated for $C_8H_{15}ON$ MR 46.63; EMR 4.63.

	Found %:	C 67.84; 67.91;	H 10.77; 10.86;	N 10.51; 10.59
$C_8H_{15}ON$.	Calculated %:	C 68.04;	H 10.70;	N 9.91

4-Diethylamino-3-buten-2-one is a yellowish oil of feeble odor, stable to storage. It dissolves in water and organic solvents. It gives a cherry-red color with ferric chloride.

The picrate was prepared in absolute alcohol and recrystallized from the same solvent: fine yellow crystals, m.p. 115-116°

	Found %:	N 15.09; 15.21
$C_{14}H_{18}O_8N_4$	Calculated %:	N 15.12

III. 4-Piperidino-3-buten-2-one

The substance was prepared according to the method of Experiment I from a solution of 38 g of piperidine in 40 ml of water and 21.0 g of 4-chloro-3-buten-2-one, the yield being 22.0 g (70%). After redistillation 4-piperidino-3-buten-2-one had the following constants: b.p. 154-155°/7 mm; d_4^{20} 1.0103; n_D^{20} 1.5730; found MR 49.97; calculated for $C_9H_{15}ON$ MR 45.05; EMR 4.92.

	Found %:	N 9.17; 8.92
$C_9H_{15}ON$.	Calculated %:	N 9.16

4-Piperidino-3-buten-2-one is a thick oil, which does not crystallize after a long freezing treatment; dissolves in water and organic solvents, and gives a cherry-red color with ferric chloride.

The picrate was prepared in absolute alcohol and recrystallized from the same solvent: large yellow crystals, m.p. 122-123°.

	Found %:	N 14.73; 14.76
$C_{15}H_{16}O_8N_4$	Calculated %:	N 14.66

IV. 1-Dimethylamino-1-hexen-3-one

1-Dimethylamino-1-hexen-3-one was prepared according to the method of Experiment I from 50 ml of a 40% aqueous solution of dimethylamine and 23.0 g of 1-chloro-1-hexen-3-one, the yield being 15.0 (61%). After redistillation 1-dimethylamino-1-hexen-3-one had the following constants: b.p. 120-121°/5 mm; d_4^{20} 0.9339; n_D^{20} 1.5364; found MR 47.18; calculated for $C_8H_{15}ON$ MR 42.63; EMR 4.55.

	Found %:	N 10.03; 9.98
$C_8H_{17}ON$.	Calculated %:	N 9.91

1-Dimethylamino-1-hexen-3-one is a yellowish oil of feeble odor, which does not change with storage, mixes with water and organic solvents, and gives a cherry-red color with ferric chloride.

V. 1-Dimethylamino-5-methyl-1-hexen-3-one

1-Dimethylamino-5-methyl-1-hexen-3-one was prepared according to the method of Experiment I from 50 ml of a 40% aqueous solution of dimethylamine and 20.5 g of 1-chloro-5-methyl-1-hexen-3-one, the yield being 14.5 g (66%). After redistillation 1-dimethylamino-5-methyl-1-hexene-3-one had the following constants:

b.p. 124-125° (4 mm); d_4^{20} 0.9245; n_D^{20} 1.5270; found MR 51.61; calculated for $C_9H_{17}ON$ MR 47.25; EMR 4.36.

Found %: N 9.42; 9.44

$C_9H_{17}ON$. Calculated %: N 9.22

1-Dimethylamino-5-methyl-1-hexene-3-one is a yellowish oil of feeble odor, soluble in water and organic solvents and giving a cherry-red color with ferric chloride.

VI. Reaction of 4-Dimethylamino-3-buten-2-one with Acetic Acid

4-Dimethylamino-3-buten-2-one (5.0 g) was heated at the boil in 10 ml of aqueous acetic acid for 20 minutes. The precipitate that formed on cooling was filtered off and recrystallized from water; it consisted of colorless needles (2.8 g, 94%), m.p. 162-163°. In admixture with 1,3,5-triacetylbenzene it showed no depression of melting point. Data in the literature for triacetylbenzene: m.p. 162-162.5° [6]; m.p. 163° [7].

SUMMARY

1. By reaction of alkyl 2-chlorovinyl ketones with secondary amines in aqueous medium, alkyl 2-dialkylaminovinyl ketones are formed in 60-85% yield. This reaction appears to be the most convenient method for the preparation of compounds of this type.

2. On the basis of an examination of the physical properties of the compounds obtained, it is concluded that their molecules have considerable polarity.

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CONDENSATION OF MESO-HALO DERIVATIVES OF 1,3-DIOXO COMPOUNDS WITH UREA

L. Sekeresh and G. Fodor

Halogen derivatives of monooxo compounds are well known starting materials for the synthesis of azoles. With amides of thiocarbonic acids [1] and with thiourea [1, 2] they give thiazole derivatives, and with carbonic acid amides they give oxazole derivatives [3]. It is interesting, however, to note that condensation with urea yields imidazole derivatives, and not an aminooxazole as might be expected.

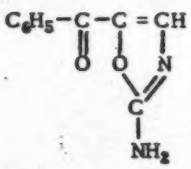
The behavior of meso-halo 1,3-dioxo compounds in such condensations has not been previously investigated. The only example described in the literature is the condensation of 3-bromo-2,4-pentanedione with 1-(N-acetylsulfanilyl)-2-thiourea, which resulted in the formation of 5-acetyl-2-(N^4-acetylsulfanilamido)-4-methylthiazole, although no proof is advanced in the patent [5] of the structure of this compound. It has been established also that a bromine atom in the meso position in 1,3-dioxo compounds splits off mainly in the form of a cation, yielding hypobromous acid [6, 7], and in other cases behaves as atomic bromine [8]. Owing to the causes indicated above, the usual metathetic reactions of halogen derivatives proceed here at very low rates [9]. It was for this reason that we considered it to be of interest to make a more extensive study of the reactions of compounds of this type, and as an example for study we chose benzoylbromoacetaldehyde, which has been prepared by Agarwal, Gupta, and Deshapande [10].

The solubility of this compound in alkali is evidence of the occurrence of aldo-enol tautomerism, though the fact that the compound reduces Fehling's solution points to the presence of a free aldehyde group. With hexamethylenetetramine it yields, in addition to an amorphous mass, a crystalline hydrobromide of hexamethylenetetramine, which is evidence of anionic elimination of bromine.

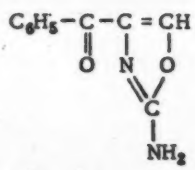
We have studied the reaction between this compound and urea. According to an empirical rule [4], which holds for α-bromo monooxo compounds, we might expect to obtain 4-benzoyl-4-imidazolin-2-one (C). On the basis, however, of the peculiar behavior of meso-halo 1,3-dioxo compounds referred to above, we must take into account the possibility of obtaining other compounds resulting from the elimination of bromine as a cation [9].

We actually found that the nitrogen compound obtained had the empirical formula $C_{10}H_8O_2N_2$ (m.p. 208-210°), and was not identical with 4-benzoyl-4-imidazolin-2-one (C) (m.p. 313°), but was an isomer of this substance. Its structure, therefore, may be represented by one of the formulas A, B, C, D, E, and F (below). Identification of the structure with one of those indicated would make it possible to obtain an idea of the reaction mechanism.

The compound obtained could not be 2-amino-5-phenyl-4-oxazolecarboxaldehyde (D) or 2-amino-4-phenyl-5-oxazolecarboxaldehyde (E), since it fails to react with dimedone. It is therefore only necessary to examine the structures A, B, and F.



(A)



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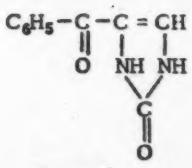
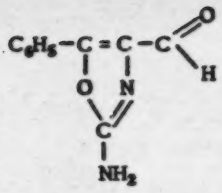
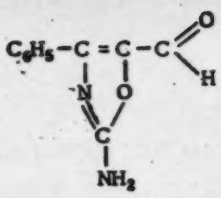


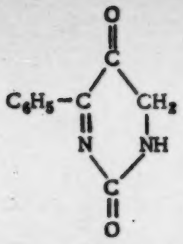
(C)



(D)

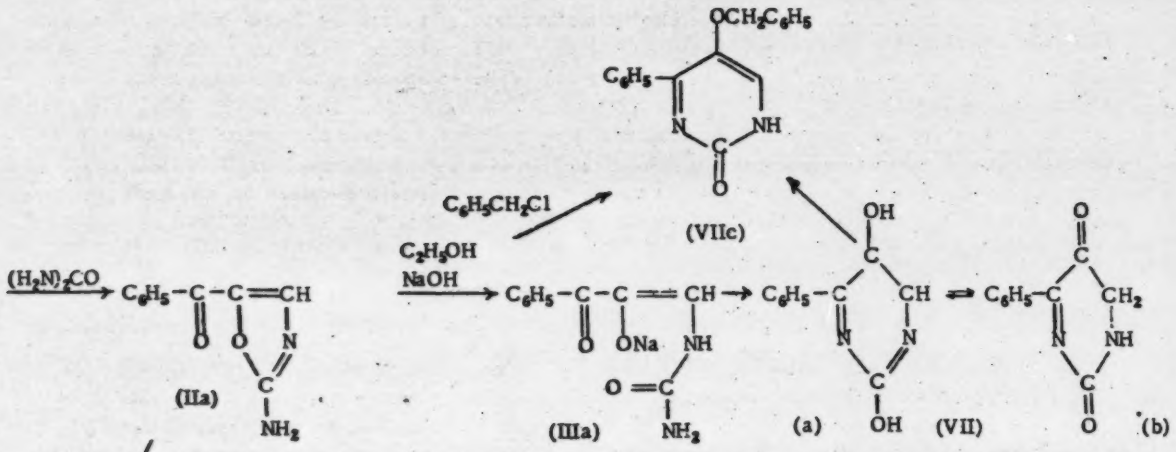


(E)

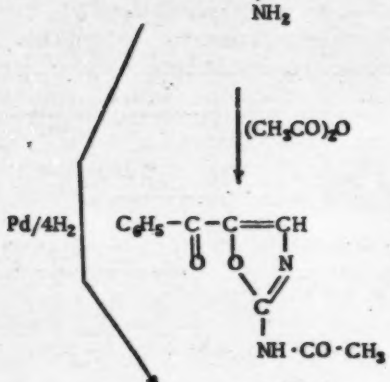


(F)

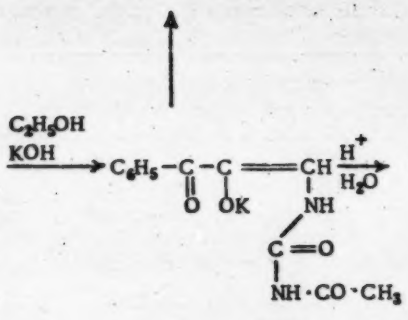
The condensation product gave a monohydrochloride and a monoacetyl derivative (IIb). By the action of caustic alkalis it was converted into a crystalline enolate, and it was found that one molecule of NaOH was taken up, so that the scission of the heterocycle must have occurred. Subsequent acidification, however, yielded not the original compound, but another, isomeric heterocycle (m.p. 320°). On the basis of a working hypothesis advanced by one of us (G. Fodor), this fact can be explained as follows: the ring of the compound first formed, i.e., 2-amino-5-benzoyloxazole (IIa), is ruptured, and the compound is converted into the Na enolate IIIa, which then, under the action of acid, forms a pyrimidine ring (see VIIa or Formula F).



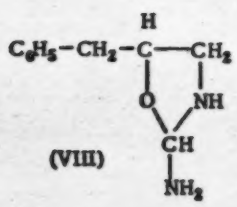
(IIa) (IIIa) (a) (VII) (b) (VIIc)



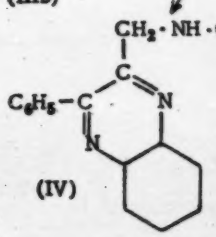
(II b)



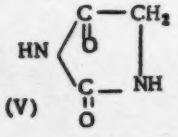
(IIIb) (IV)



(VIII)



(IV)



(V)

Although the melting point of this compound is close to that of 4-benzoyl-4-imidazolin-2-one (C), its diacetyl derivative melts at 83-84°, as compared with 139°, the melting point of the diacetyl derivative of the imidazolinone; these compounds are therefore not identical. Incidentally, such high melting points are characteristic of pyrimidinol and imidazolinone derivatives.

In order to substantiate this hypothesis, we attempted to convert the supposed pyrimidine derivative by chlorination and subsequent reductive dehalogenation into the corresponding bisdesoxy compound, i.e., 4-phenylpyrimidine, which could be synthesized also by another means [12]. Chlorination, however, did not yield a homogeneous product, and the problem was therefore tackled in another way.

It was proved that the oxygen atom in the ring of the heterocyclic compound IIa (oxazole derivative) first formed corresponds to the oxygen atom of the enol group of the salt IIIa formed by the action of alkali. On treatment of the Na enolate with benzyl chloride, it was converted not into a benzyl derivative of the original compound, but into a monobenzyl ether (VIIc) of the compound $C_{10}H_8O_2N_2$ (pyrimidine derivative), which has an acid character. It was found possible to obtain this ether also by the action of benzyl chloride on the above-mentioned high-melting compound (VIIa). It follows that the enol hydroxyl group does not participate in the second ring closure.

In subsequent work, therefore, we tried to prove the structure of the primary condensation product. First of all, we tried hydrogenation with the object of converting the condensation product into a known amino-1-phenylpropanediol and studying its structure. On hydrogenation in presence of palladium, however, the substance took up only four molecules of hydrogen with loss of one of its oxygen atoms, being converted into a compound of formula $C_{10}H_{14}ON_2$ (probably VIII), a compound which was very stable toward alkalis and acids; it did not enable us to draw any conclusion concerning the structure of the original compound. We therefore directed our attentions to a more thorough study not of the primary condensation product, but of its N-monoacetyl derivative (IIb). Under the action of alcoholic KOH, this monoacetyl derivative combined with one molecule of KOH, yielding a crystalline K enolate with simultaneous rupture of the heterocycle. This process was found to be reversible, IIb being re-formed on acidification. The N-acetylated product was not converted into a secondary heterocyclic compound of acidic character, but into the free base. This fact indicated that the nitrogen atom took part in the formation of the molecule of the secondary heterocyclic product, but not in the formation of the primary product IIa.

When a solution of the K enolate IIb in 10% alcohol was treated with hydrochloric acid, and the mixture highly diluted with water, ring closure with formation of the original compound, did not occur, but the crystalline product IV separated. The 1,2-dioxo structure of this was proved as follows: 1) with o-phenylenediamine a quinoxaline derivative (VI) was obtained; 2) on being oxidized with metaperiodic acid, it broke down to give benzoic acid and hydantoin (V).

Our supposition that the structure of the compound obtained from benzoylbromoacetaldehyde and urea corresponds to Formula A, and not Formula B, was therefore confirmed. The isomeric compound obtained from it in the secondary ring closure can be only F, since the compounds C, D, and E have been altogether excluded. The diketo compound, on being warmed with hydrochloric acid is converted into the pyrimidine VII, thus proving the structure of the latter.

As a result of these proofs we may conclude that in the reaction of the meso-halo 1,3-dioxo compound studied with urea the oxygen atom of the urea molecule attacks the carbon atom linked to bromine, whereas the nitrogen atom of the imino group reacts with the carbon atom linked to the hydroxyl group of the aldo-enol system.

Such a reaction mechanism is reminiscent of that for the reaction between α-halo monooxo compounds and thiourea [2], and is not analogous to the formation of imidazolinones [4] in the reaction of α-halo monooxo compounds with urea. On the other hand, the high rate of the reaction studied is evidence in favor of the view that a halogen atom in the meso position is, contrary to expectation [9], readily eliminated in the form of an anion.

EXPERIMENTAL

Reaction of Benzoylbromoacetaldehyde with Hexamethylenetetramine. Hexamethylenetetramine (1.4 g) was dissolved in 15 ml of absolute chloroform, and benzoylbromoacetaldehyde (2.3 g) dissolved in 35 ml of absolute chloroform was added. After a few minutes, a white crystalline precipitate formed in the solution. The precipitate was filtered off, washed with chloroform, and dried, yielding 1.5 g of white crystals, m.p. 190-191°.

Delepine [13] gives the same melting point.

Found %: N 25.40; Br 36.00
$C_6H_{12}N_4HBr$. Calculated %: N 25.30; Br 36.20

The mother liquor was carefully evaporated at not above 50°, but no homogeneous compound could be obtained from the residue.

2-Amino-5-benzoyloxazole (IIa). Benzoylbromoacetaldehyde [10] (12 g; m.p. 110°) was dissolved in 250 ml of acetone, and urea (8 g) was added The reaction mixture was boiled for 40 minutes on a water bath, when all the urea dissolved. Acetone (about 200 ml) was driven off, and the remaining solution, which was of a red color, was poured with continuous stirring into water (1 liter). An oil, which solidified forming yellowish crystals (8.3 g; m.p. 180-200°), was precipitated.

Recrystallization of the crude product from ten times its weight of ethanol yielded yellowish crystals (about 50% of the crude product), m.p. 208-210°. This compound was soluble in dilute hydrochloric acid and, when warmed slightly, in 2 N NaOH.

Found %: C 63.87; H 4.19; N 15.39
$C_{10}H_8O_2N_2$. Calculated %: C 63.77; H 4.29; N 14.88

The crude product was dissolved in twice its weight of 18% hydrochloric acid on a water bath and filtered. Concentrated ammonia was then added to a weakly alkaline reaction. The product purified in this way also melted at 208-210°.

Its Hydrochloride. 2-Amino-5-benzoyloxazole (0.9 g) was heated on a water bath with 25 ml of 20% hydrochloric acid until solution was complete, and the mixture was then evaporated under reduced pressure. The residual crystalline mass was recrystallized from 10 ml of ethanol, yielding 0.25 g of the hydrochloride, m.p. 198-200°.

Found %: C 53.86; H 4.38; N 12.13; Cl 15.89
$C_{10}H_9O_2N_2Cl$. Calculated %: C 53.46; H 4.03; N 12.47; Cl 15.78

Its Acetyl Derivative (IIb). 2-Amino-5-benzoyloxazole (0.9 g) was dissolved in 5 ml of acetic anhydride, and the mixture was heated under reflux for one hour. On the next day crystals separated from the mixture; they were filtered off and washed with ethyl acetate The yield of crystals (m.p. 189-191°) was 0.55 g. The melting point of a mixture with IIa was 163°.

Found %: C 62.13; H 4.52; N 12.32
$C_{12}H_{10}O_3N_2$. Calculated %: C 62.60; H 4.37; N 12.16

The Transformations IIb → IIIb → IIb. The acetyl derivative IIb was dissolved in a hot 10% alcoholic solution of KOH, giving a solution from which a K enolate crystallized out on cooling. The solution was diluted with water and acidified to Congo red with hydrochloric acid. The crystals that separated melted at 185-188°, and in admixture with the original substance showed no depression in melting point.

Catalytic Hydrogenation of IIa and IV. a) 2-Amino-5-benzoyloxazole (IIa; 2 g) was dissolved in 100 ml of 96% ethanol and, after addition of 1 ml of a 20% solution of dry HCl in alcohol, was hydrogenated in presence of 0.5 g of palladized bone charcoal (20% Pd), 845 ml of hydrogen being absorbed in 145 minutes (4 moles of H_2 = 950 ml). The alcoholic solution was evaporated under reduced pressure, and an amorphous residue (2 g) remained which whenrubbed out with 10 ml of water yielded 1.5 g of a white crystalline compound, m.p. 133-143°. Recrystallization from 40 ml of ethyl acetate yielded 0.95 g of a substance, m.p. 146-148°. According to its molecular formula this compound is either 2-amino-5-benzoyloxazolidine (VIII) or an isomer of this substance, (3-phenylpropyl)urea.

Found %: C 67.44; H 8.01; N 15.2
$C_{10}H_{14}ON_2$. Calculated %: C 67.38; H 7.92; N 15.72

b) 3-(3-Acetylureido)-1-phenyl-1,2-propanedione (IV; 2.5 g) was dissolved in 120 ml of alcohol and, after addition of 4 ml of a concentrated solution of dry HCl in alcohol, was hydrogenated in presence of 0.5 g of palladized bone charcoal (20% Pd), 750 ml of hydrogen being absorbed in 145 minutes. The colorless alcoholic solution was evaporated down, and the oil remaining was rubbed out with 50 ml of water, yielding a crystalline product (0.6 g). Recrystallization from a small amount of ethyl acetate yielded 0.4 g of a substance of m.p. 146-148°. This product showed no depression in melting point when mixed with the product of the hydrogenation of 2-amino-5-benzoyloxazole.

In order to study the structure of this hydrogenation product, experiments were made on its splitting by acids and alkalis: 1) The hydrogenation product (0.5 g) was boiled with 25 ml of 20% hydrochloric acid for nine hours, and on the next day the solution was evaporated down under reduced pressure and the residue was rubbed out with a small amount of water, yielding 0.3 g of a product of m.p. 144-146°, which showed no depression in melting point when mixed with the original substance. 2) The hydrogenation product (0.5 g) was boiled with 10 ml of 20% KOH solution for three hours under reflux. The solution was cooled, and white crystals separated (0.35 g; m.p. 143-145°) which showed no depression in melting point when mixed with the original substance.

Sodium Salt of the Enolate of 1-Phenyl-3-ureido-1,2-propanedione (IIIa). 2-Amino-5-benzoyloxazole (1 g) was dissolved in warm 5% aqueous NaOH, and when the solution was cooled 0.5 g of yellow crystals separated.

Found %: N 12.27; Na 11.32
$C_{10}H_9O_3N_2Na$. Calculated %: N 12.29; Na 10.08

4-Phenyl-2,5-pyrimidinediol (VII). 2-Amino-5-benzoyloxazole (1.5 g) was dissolved under slight warming in 25 ml of 2 N KOH. The hot solution was filtered and acidified with 15 ml of concentrated hydrochloric acid, when an oil separated that immediately solidified. The yellow crystals (1.5 g) obtained decomposed at about 250°. The substance was recrystallized from 75 ml of glacial acetic acid. The product (0.7 g; dec. 320°) was readily soluble in alkalis in the cold.

Found %: C 63.48; H 4.30; N 14.39
$C_{10}H_8O_2N_2$. Calculated %: C 63.83; H 4.55; N 14.89

Its Diacetyl Derivative. 4-Phenyl-2,5-pyrimidinediol (0.5 g) was dissolved in 10 ml of warm acetic anhydride. The solution was boiled for two hours, cooled, and then poured onto 100 g of ice. The oily product that separated was recrystallized from a mixture of water and acetone (one day was required), yielding dark yellow crystals, m.p. 83-84°.

Found %: C 61.12; H 4.31; N 10.34
$C_{14}H_{12}O_4N_2$. Calculated %: C 61.78; H 4.44; N 10.29

Its Monobenzyl Ether (VIIc). Benzyl chloride (2 ml) was dissolved in 10 ml of dry commercial xylene, and the sodium salt of the enolate of 1-phenyl-3-ureido-1,2-propanedione (1.5 g), ground to a powder, was added. The suspension was boiled for eight hours and then cooled. The crystals were filtered off, repeatedly washed with benzene, and then boiled with 25 ml of water. Inorganic salts were thus removed, and a yellowish crystalline mass (1 g) remained. Recrystallization from methanol yielded 0.3 g of 4-phenyl-2,5-pyrimidinediol, which decomposed at 320° (% N found: 14.91).

From the mother solution of pyrimidine derivative, yellow crystals (0.35 g), m.p. 198-200°, separated. These, according to analysis, consisted of the monobenzyl ether of 4-phenyl-2,5-pyrimidinediol.

Found %: C 73.31; H 4.97; N 10.02
$C_{17}H_{14}O_2N_2$. Calculated %: C 73.38; H 5.07; N 10.07

This compound is insoluble in hydrochloric acid; it dissolves readily in alkalis, but is reprecipitated by hydrochloric acid.

Acid Hydrolysis of the Monobenzyl Ether. The substance VIIc (0.3 g) was boiled for five hours with 5 ml of hydrobromic acid dissolved in glacial acetic acid, and the mixture was poured into 200 ml of water. The amorphous substance that separated was rubbed out with methanol, yielding a crystalline compound, m.p. 320°, which showed no depression in melting point when mixed with 4-phenyl-2,5-pyrimidinediol (VIIa).

Found %: N 14.79
Calculated %: N 14.89

Potassium Salt of the Monoenolate of 3-(3-Acetylureido)-1-phenyl-1,2-propanedione (IIIb). 2-Acetamido-5-benzoyloxazole (IIb; 2.5 g) was suspended in 20 ml of alcohol, and a solution of 0.61 g of KOH in a mixture of 1 ml of water and 5 ml of ethanol was added. At first a clear solution was obtained, and then the potassium salt was rapidly precipitated. The mixture was cooled with ice, and the substance was filtered off and washed several times. The product (1.75 g) consisted of yellow crystals of good solubility in water.

Found %: N 10.61; K 14.05
$C_{12}H_{11}O_4N_2K$. Calculated %: N 9.79; K 13.64

3-(3-Acetylureido)-1-phenyl-1,2-propanedione (IV). A solution of 1.8 g of KOH in 3 ml of water was added to a suspension of 7.5 g of 2-acetamido-5-benzoyloxazole (IIb) in 250 ml of warm ethanol. The substance dissolved, and the solution was diluted with 2000 ml of water and acidified with 50 ml of concentrated hydrochloric acid. After several hours the diketone began to separate from the solution in the form of light crystals. After one day the crystals were filtered off and dried (3 g); they were yellowish green and melted with decomposition at 214-224°. Recrystallization from methanol yielded glistening plates, m.p. 230° (dec.).

Found %: C 58.46; H 4.46; N 11.29
$C_{12}H_{12}O_4N_2$. Calculated %: C 58.06; H 4.84; N 11.28

2-(3-Acetylureidomethyl)-3-phenylquinoxaline (VI). 3-(3-Acetylureido)-1-phenyl-1,2-propanedione (50 mg) was dissolved in 5 ml of alcohol and 50 mg of a concentrated aqueous solution of o-phenylenediamine was added. The mixture was heated for a short time on a water bath, and white woolly needles separated, m.p. 268-270°.

Found %: C 67.52; H 5.38; N 16.90
$C_{18}H_{16}O_2N_4$. Calculated %: C 67.50; H 5.00; N 17.50

Hydantoin (V). To a suspension of 0.5 g of 3-(3-acetylureido)-1-phenyl-1,2-propanedione (IV) in 15 ml of dioxane, a solution of 0.45 g of metaperiodic acid in 3 ml of water was added. The mixture darkened, and the suspended substance went into solution with rise in temperature. The mixture was allowed to stand for 15 minutes and then neutralized to litmus with 2 N KOH. The solid substance obtained was filtered off and rubbed out with an absolute alcoholic solution of HCl. The salt formed was filtered off, and the alcoholic mother liquor was diluted with a few milliliters of alcohol and evaporated under reduced pressure. The somewhat dark colored residue was dissolved in acetone and separated from inorganic products by filtration. The acetone filtrate was evaporated down and the residue rubbed out with a small amount of water, yielding 40 mg of a white crystalline compound of m.p. 218-221°. Lippmann [14] gives 220-221° for the melting point of hydantoin.

Found %: C 35.15; H 4.09; N 28.24
$C_3H_4O_2N_2$. Calculated %: C 36.00; H 4.00; N 28.00

The product in admixture with hydantoin prepared from hydantoic acid showed no depression in melting point.

The dioxane mother liquor was evaporated under reduced pressure, and the residual crystalline mass was dissolved successively in alcohol and in concentrated aqueous hydrochloric acid, dissolution being followed in each case by evaporation. The dark colored residue was recrystallized from 50% aqueous alcohol, and the product consisted of crystals, m.p. 118-121°, which showed no depression in melting point when mixed with benzoic acid.

* * *

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HIGH TEMPERATURE CATALYTIC DEHYDROGENATION OF ETHYLCYCLOHEXANE

COMMUNICATION 1. MAIN DIRECTION OF THE REACTION

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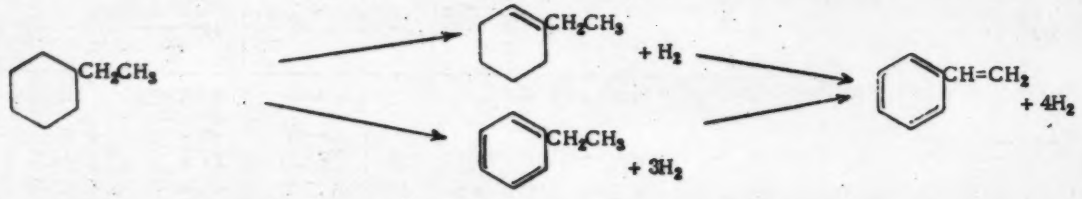
The dehydrogenation of cyclohexane hydrocarbons in presence of oxide catalysts was first described in the literature by Balandin and Brusov [1] and Moldavsky and coworkers [2]. In these investigations studies were made of the properties of catalysts consisting of oxides of chromium, molybdenum, aluminum, zinc, magnesium, and other metals. It was then established that at 410-440° the dehydrogenation of cyclohexane to benzene could proceed to the extent of 74-77%. In later investigations, however, other workers have shown that the main reaction of dehydrogenation of hydroaromatic hydrocarbons to the corresponding aromatic compounds is accompanied by the formation of intermediate substances and by-products. Plate and Tarasova [3] studied the dehydrogenation of cyclohexane in presence of an aluminum/vanadium oxide catalyst, and in the catalyzates obtained at 500° they found 3.5% of cyclohexene, which they isolated as its insoluble compound with a mercury salt. Herington and Rideal [4] studied the kinetics of dehydrogenation of cyclohexane and its homologs at 450° in presence of an aluminum/chromium oxide catalyst, and they concluded from an analysis of the results that the unsaturated hydrocarbons formed consisted mainly of cycloalkenes, which were intermediate products in the dehydrogenation of hydroaromatic hydrocarbons. There are no indications in the literature of the formation of cyclohexadiene in the dehydrogenation of cyclohexane in presence of oxide catalysts; on the contrary, the absence of this hydrocarbon in the catalyzates has been pointed out [4,5] *.

The catalytic dehydrogenation of ethylbenzene has been investigated by Zelinsky, Balandin, and coworkers [8], Sergienko [9], and Zalkind and Bulavsky [10,11]. This reaction develops at 500-600° in presence of catalysts of approximately the same composition as those used in the dehydrogenation of hydroaromatic hydrocarbons (oxides of Cr, V, Al, Mg, Zn, etc.). Dilution of ethylbenzene with inert gases (CO_2, N_2) considerably increases the yield of styrene.

On the basis of these data from the literature, it might be expected that the main direction of the dehydrogenation of ethylcyclohexane in presence of oxide catalysts at 500-600° would be that leading to the formation of ethylbenzene and styrene. The formation of vinylcyclohexane does not appear very likely. Sergienko [12] showed that passage of vinylcyclohexene over chromic oxide at 400° resulted in its almost complete (99%) conversion into ethylbenzene. These reaction routes for the dehydrogenation of ethylcyclohexane may be represented by the following scheme.



* It may be mentioned that the dehydrogenation of hydroaromatic hydrocarbons by Zelinsky's method is carried out at a lower temperature (300°) in presence of metal catalysts (Pt, Pd, Ni); the corresponding aromatic hydrocarbon is then obtained, the formation of by-products or intermediate substances not generally being observed [6,7].

The high temperature catalytic dehydrogenation of ethylcyclohexane has been investigated by Herington and Rideal [4]. The only result of this investigation cited by the authors is the ratio styrene/ethylbenzene in the ethylcyclohexane catalyzate. Unfortunately, the authors do not give many of the fundamental data (space velocities for ethylcyclohexane, styrene and ethylbenzene contents of the catalyzates, method used for the analysis of the catalyzates, etc.), thus lowering the value of this part of the work. In the present investigation the dehydrogenation of ethylcyclohexane has been studied in presence of two catalysts for the passage of ethylcyclohexane or a mixture of its vapor with carbon dioxide at various molar velocities over the catalyst. For comparison, the dehydrogenation of ethylbenzene was studied under analogous conditions.

EXPERIMENTAL

Experimental Procedure

Apparatus and Experimental Method. This is described in a previous paper [13]. Experiments on the dehydrogenation of ethylcyclohexane were alternated with experiments on the dehydrogenation of ethylbenzene. After each experiment the catalyst was regenerated in a current of air so as to preserve constant catalyst activity. In the course of an experiment, 20-25 ml of hydrocarbon was passed. The molar velocity was taken as a fundamental parameter so that it would be possible to compare the results of experiments in which the substances to be dehydrogenated were diluted with carbon dioxide with the results obtained without dilution (changes in molar velocity are inversely proportional to changes in time of contact). The unit adopted for molar velocity was one mole of original substance (or substances) passing per hour over one liter of catalyst, space velocities being expressed in liters of liquid substance passing per hour over one liter of catalyst. The degree of dilution of ethylcyclohexane and ethylbenzene vapors was determined from the ratio of the molar velocity of carbon dioxide to that of the substance being dehydrogenated; it was approximately constant (about 2) in all experiments.

Starting Materials. The ethylbenzene boiled (over sodium) over the range 135.9-136.1° and had n_D^{20} 1.4966 and d_4^{20} 0.8664. The literature [14] gives b.p. 136.1°, n_D^{20} 1.4959 and d_4^{20} 0.8669. Ethylcyclohexane was prepared by the hydrogenation of ethylbenzene in presence of a nickel catalyst under 70-100 atm at 130°. The ethylcyclohexane so prepared was treated twice with concentrated sulfuric acid, washed with water, and dried over $CaCl_2$. On being distilled over sodium through a column of 19 theoretical plates, it came over in the range 130.0-130.2° and had n_D^{20} 1.4340 and d_4^{20} 0.7848. The literature [14] gives b.p. 130.4°, n_D^{20} 1.4332 and d_4^{20} 0.7848. The carbon dioxide was passed through a train of two wash bottles of 10% sodium carbonate solution, a calcium chloride tube, and a rheometer, from which it passed to the reaction tube.

Analysis of Catalyzates. The contents of unsaturated substances in the ethylcyclohexane dehydrogenation catalyzates were determined by Rosenmund's bromometric titration method [15]. Investigation of the ethylcyclohexane catalyzates by the polymerization method (see below) showed that the unsaturated hydrocarbons formed consisted essentially of styrene. In the bromometric calculations, therefore, the molecular weight of styrene was employed.

TABLE 1

Check of the Sulfuric Acid Absorption Method

Expt. No.	Composition of artificial mixture (wt. %)			Amount of mixture taken (g)	Residue of cyclohexane (g)	n_D^{20} of the residue	Ethylcyclohexane content by analysis (wt. %)	Discrepancy (%)
	Styrene	Ethylbenzene	Ethylcyclohexane					
7	14.3	12.6	73.1	7.98	5.7	1.4370	71.3	−1.8
7'	14.3	12.6	73.1	7.99	5.8	1.4376	72.5	−0.6
8	13.5	13.3	73.2	8.17	5.8	1.4340	71.0	−2.2
8'	13.5	13.3	73.2	7.94	5.5	1.4338	69.4	−3.8
6	23.2	21.3	55.5	8.22	4.3	1.4340	52.3	−3.2
6'	23.2	21.3	55.5	8.19	4.7	1.4483	57.5	+2.0
9	20.9	25.4	53.7	8.15	4.3	1.4438	52.8	−0.9
9'	20.9	25.4	53.7	8.19	4.6	1.4475	56.2	+2.5

The contents of unchanged ethylcyclohexane in the catalyzates were determined from the amount of the residue after absorption of unsaturated hydrocarbons and ethylbenzene with concentrated sulfuric acid (monohydrate). In order to avoid heating and polymerization of styrene when performing this operation, a cylinder containing a quantity of monohydrate (10 ml) and a weighed amount of catalyzate (volume 10 ml) was cooled to −10-15°. The cylinder was then shaken carefully and again cooled, after which shaking was continued in a mechanical shaker. After separation of the sulfuric acid layer, the operation was repeated, the only difference being that the quantity of monohydrate taken was 5 ml. This method was checked on mixtures of styrene, ethylbenzene, and ethylcyclohexane. The results of these checks are given in Table 1.

The weight of residue was determined from its volume and the specific gravity of ethylcyclohexane. The refractive indices of the residues were somewhat greater than the value for ethylcyclohexane, probably owing to the presence of sulfonation of polymerization products. The difference between true and found content of ethylcyclohexane in the mixture did not exceed 3.8%.

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/Chromium/Molybdenum Oxide Catalyst

The dehydrogenation of ethylcyclohexane in presence of an aluminum/chromium/molybdenum oxide catalyst was carried out at 495° in presence of carbon dioxide as diluent. The results of this series of experiments are given in Table 2 and Fig. 1.

A four-fold increase in the total molar velocity of ethylcyclohexane and carbon dioxide (from 1.7 to 7.1) led to a reduction in the ethylbenzene content of the ethylcyclohexane catalyzate from 55.5% to 26.5%, but had no effect on the content of unsaturated hydrocarbons (5-6%).

TABLE 2

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/Chromium/Molybdenum Oxide Catalyst at 495° in Presence of Carbon Dioxide as Diluent

Expt. No.	Hydrocarbon being dehydrogenated	Space velocity (liter/liter-hr)	Molar velocity (mole/liter-hour)			Degree of dilution	Yield of catalyzate (wt.% on HC passed)	Content in catalyzate of reaction products (wt.%)	
			Hydrocarbon	CO_2	Total			Unsaturated hydrocarbon (styrene)	Ethylbenzene
56	Ethylcyclohexane	0.08	0.6	1.1	1.7	1.8	70	5.0	55.5
60	"	0.14	1.0	2.0	3.0	2.0	63	6.0	42.5
62	"	0.22	1.6	3.2	4.8	2.0	63	4.9	29.1
52	"	0.30	2.1	5.0	7.1	2.4	81	5.2	26.5
57	Ethylbenzene	0.09	0.8	1.1	1.9	1.4	74	19.2	—
59	"	0.12	1.0	2.0	3.0	2.0	83	23.3	—
58	"	0.19	1.5	3.4	4.9	2.3	84	22.2	—
53	"	0.30	2.5	5.0	7.5	2.0	86	19.9	—

Change, over approximately the same range, in the molar velocities of ethylbenzene and CO_2 was also practically without effect on the styrene content of the catalyzate (19.2-23.3%).

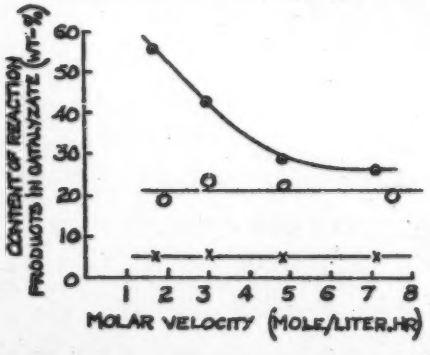


Fig. 1. Dehydrogenation of ethylcyclohexane and ethylbenzene in presence of an aluminum/chromium/molybdenum oxide catalyst at 495° in presence of carbon dioxide as diluent:
× – unsaturated substances from ethylcyclohexane;
● – ethylbenzene from ethylcyclohexane;
○ – styrene from ethylbenzene.

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/ Vanadium Oxide Catalyst

All experiments in presence of an aluminum/ vanadium oxide catalyst were carried out at 547°. The dehydrogenation of ethylcyclohexane and ethylbenzene was performed both in presence of carbon dioxide as diluent for the vapor of the reactant, and also in absence of diluent.

The results of experiments on the dehydrogenation of ethylcyclohexane and ethylbenzene over an aluminum/ vanadium oxide catalyst in presence of carbon dioxide as diluent are given in Table 3 and Fig. 2. Rise in temperature led to increase in the concentrations of reaction products in the catalyzates. Change in the total molar velocities of ethylcyclohexane and CO_2 over the same range (1.7 to 7.2) as before led to a reduction of the ethylbenzene content of the ethylcyclohexane catalyzates from 67.5% to 38.9%, but was accompanied by the formation of practically unchanged amounts of unsaturated hydrocarbons (10.4-13.9%).

The styrene content of the catalyzates from the dehydrogenation of ethylbenzene in presence of CO_2 also remained practically constant (28.6-31.1%) as the total molar velocity changed from 1.6 to 7.3; the somewhat higher degree of dehydrogenation in Expt. 104 resulted probably from an increase in the degree of dilution to 2.4.

TABLE 3

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/ Vanadium Oxide Catalyst at 547° in Presence of Carbon Dioxide as Diluent

Expt. No.	Hydrocarbon being dehydrogenated	Space velocity (liter/ liter-hr)	Molar velocity (mole/ liter-hour)			Degree of dilution	Yield of catalyzate (wt.% on HC passed)	Content in catalyzate of reaction products (wt %)	
			Hydrocarbon	CO_2	Total			Unsaturated hydrocarbon (styrene)	Ethylbenzene
72	Ethylcyclohexane	0.08	0.6	1.1	1.7	1.8	80	12.3	67.5
75	"	0.13	0.9	2.0	2.9	2.1	77	13.9	62.5
78	"	0.22	1.5	3.0	4.5	2.0	85	11.6	52.8
71	"	0.31	2.2	5.0	7.2	2.3	86	10.4	38.9
76	Ethylbenzene	0.06	0.5	1.1	1.6	2.2	74	28.6	–
74	"	0.12	1.0	2.0	3.0	2.0	83	29.5	–
79	"	0.29	2.4	5.0	7.4	2.1	89	31.1	–
70	"	0.30	2.4	5.0	7.4	2.1	89	29.9	–
104	"	0.26	2.2	5.1	7.3	2.4	81	35.3	–

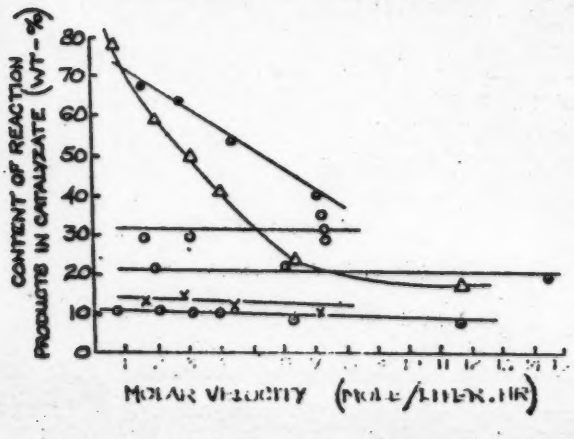


Fig. 2. Dehydrogenation of ethylcyclohexane and ethylbenzene in presence of an aluminum/ vanadium oxide catalyst at 547°:

X – unsaturated substances from ethylcyclohexane (CO_2 diluent);

⊖ – ethylbenzene from ethylcyclohexane (CO_2 diluent);

O – styrene from ethylbenzene (CO_2 diluent);

⊙ – unsaturated substances from ethylcyclohexane (no diluent);

△ – ethylbenzene from ethylcyclohexane (no diluent);

◑ – styrene from ethylbenzene (no diluent).

The dehydrogenation of ethylcyclohexane and ethylbenzene in absence of diluent was carried out with the same portion of aluminum/ vanadium oxide catalyst. The results of these experiments are given in Table 4. An approximately seventeenfold increase in the molar velocity of ethylcyclohexane (from 0.7 to 11.7) resulted in a reduction in the ethylbenzene content of the catalyzates from 78.6% to 17.4%, whereas the concentration of unsaturated substances diminished only from 10.4% to 7.3%. There was a similar small change in the styrene content of the ethylbenzene dehydrogenation catalyzate (from 20.7% to 18.8%) for a change in molar velocity from 2.0 to 14.5.

TABLE 4

Dehydrogenation of Ethylcyclohexane and Ethylbenzene in Presence of an Aluminum/ Vanadium Oxide Catalyst at 547°, No Diluent Being Present

Expt. No.	Hydrocarbon being dehydrogenated	Space velocity (liter/ liter-hr)	Molar velocity (mole/ liter-hr)	Yield of catalyzate (wt.% on HC passed)	Content in catalyzate of reaction products (wt.%)	
					Unsaturated hydrocarbon	Ethylbenzene
99	Ethylcyclohexane	0.11	0.7	67	10.4	78.6
98	"	0.29	2.0	77	11.1	58.9
100	"	0.45	3.1	85	9.9	49.6
101	"	0.56	4.0	83	9.9	40.6
133	"	0.90	6.3	93	8.0	23.6
134	"	1.67	11.7	92	7.3	17.4
103	Ethylbenzene	0.24	2.0	87	20.7	—
97	"	0.76	6.2	93	23.0	—
102	"	1.75	14.5	94	18.8	—

A comparison of the results of these series of experiments (with and without a carbon dioxide diluent; see Fig. 2) shows that an equal dilution of ethylcyclohexane vapor and ethylbenzene vapor leads to the same relative increase in the concentration of unsaturated hydrocarbons (styrene). At the dilution investigated (about 2), the concentrations of unsaturated substances in the ethylcyclohexane catalyzates and of styrene in the ethylbenzene catalyzates increased by about 30%: the styrene concentration in the ethylbenzene catalyzates was 18.8-23.0% in absence of diluent and 28.6-31.1% in presence of diluent; the concentration of unsaturated hydrocarbons in the ethylcyclohexane catalyzates was 7.3-11.1% without diluent and 10.4-13.9% qith diluent. The reduction in the degree of dehydrogenation of ethylcyclohexane to ethylbenzene in experiments without diluent, as compared with the experiments in which a carbon dioxide diluent was used, is to be explained, evidently, by a certain loss in catalyst activity with respect to the dehydrogenation of the cyclohexane ring. The activity of the catalyst for the dehydrogenation of ethylbenzene to styrene remained practically constant, as will be seen by a comparison of the results of Expts. 70 and 104 (Table 3), which were performed at the beginning and end, respectively, of the trials with the given portion of catalyst.

Determination of Styrene in Ethylcyclohexane Catalyzates by the Polymerization Method

It was pointed out above that the content of unsaturated hydrocarbons in ethylcyclohexane catalyzates was determined by bromometric titration. The high concentrations of ethylbenzene in these catalyzates gave reason to suppose that the unsaturated hydrocarbons formed consisted essentially of styrene. It was necessary to determine, however, whether any other unsaturated hydrocarbons were formed. For this purpose the ethylcyclohexane catalyzates were investigated by the polymerization method. Marukyan [16] has examined the applicability of the bromometric titration and polymerization methods for the determination of styrene and has found good agreement (within 1%) between the results obtained by these methods. In one of our previous investigations [17] we obtained similar results. On the other hand, there is nothing in the literature concerning the tendency of cyclohexene or ethylcyclohexene to polymerize. The tendency of vinylcyclohexane to polymerize (under prolonged treatment at 170°) was investigated by Shorygin and Shorygina [18]: the authors concluded that this hydrocarbon is not able to polymerize and shows only an "incipient" tendency to form dimers. The polymerization method, therefore, has enabled more accurate results to be obtained for the styrene contents of the catalyzates than could be obtained by bromometric titration.

The ethylcyclohexane catalyzates obtained in the experiments with an aluminum/vanadium oxide catalyst at 547° in absence of diluent (see Table 4) were united. The united catalyzate contained 9.0% of unsaturated hydrocarbons (calculated as styrene) as determined by bromometric titration. A 31.2 g sample of the united catalyst, with an addition of 0.4 g of benzoyl peroxide, was sealed in a tube and maintained at 150-160° for 80 hours, after which it was fractionated at 50 mm pressure. The fractionation yielded 2.3 g of solid polymer (instead of the calculated 2.8 g) and 28.3 g nonpolymerized catalyzate. The amount of polymer obtained was 6.1% of weight of catalyzate taken (after making a correction for the added benzoyl peroxide). It follows from these results that the united catalyzate contained 6.1% of styrene and 2.9% of other, nonpolymerizing unsaturated hydrocarbons. The content of the latter was determined also by another method. The nonpolymerizing part of the catalyzate, which was distilled from the polymer at 50-60° and 50 mm pressure, had n_D^{20} 1.4560 and contained 38% of ethylbenzene and 4.5% of unsaturated hydrocarbons. This content of nonpolymerizing unsaturated hydrocarbons in the distillate corresponds to 4.1% of them in the united catalyzate.

The liquid distilled from the polymer was treated with monohydrate in order to remove aromatic and unsaturated hydrocarbons. The residue obtained contained no unsaturated substances, distilled over Na at 130-131°, and had d_4^{20} 0.7867 and n_D^{20} 1.4321. These constants are close to those of ethylcyclohexane (b.p. 130.4°, d_4^{20} 0.7840 and n_D^{20} 1.4332) [14], and they indicate that very little destructive decomposition of ethylcyclohexane occurs in the course of its dehydrogenation. The nonpolymerizing unsaturated hydrocarbons were therefore formed by the dehydrogenation of ethylcyclohexane, and probably consisted of ethylcyclohexene.

The united ethylcyclohexane catalyzate, therefore, contained 6.1% of styrene and 3-4% of unsaturated hydrocarbons of different character. The unsaturated part of the united catalyzate consisted, therefore, of about 65% of styrene and about 35% of nonpolymerizing unsaturated hydrocarbons. It follows from a comparison of these results with those described previously that the main direction of the dehydrogenation of ethylcyclohexane is that leading to the formation of ethylbenzene and styrene, the reaction being accompanied, however, by the formation of small amounts of unsaturated hydrocarbons of another character.

DISCUSSION OF RESULTS

The main products of the high temperature catalytic dehydrogenation of ethylcyclohexane are ethylbenzene and styrene. The ethylbenzene content of the ethylcyclohexane catalyzates rapidly falls as the molar velocity rises, but the concentration of unsaturated hydrocarbons (which consist mainly of styrene) remains practically constant. The styrene content of the catalyzates from the dehydrogenation of ethylbenzene also remains practically unchanged as the molar velocity varies over a wide range, and it is several times as great as the concentration of unsaturated hydrocarbons in the ethylcyclohexane catalyzates.

The results obtained permit us to conclude that the dehydrogenation of ethylcyclohexane proceeds in two stages:

ethylcyclohexane → ethylbenzene → styrene.

The question arises, however, of the causes of the nondependence of styrene formation from ethylcyclohexane on the degree of aromatization of ethylcyclohexane. It is interesting to note that other investigators have observed a constant concentration of cyclohexene in catalyzates from cyclohexane having different degrees of aromatization. Plate and Druzhchits [5], for example, studied the reactions of cyclohexane and cyclohexane-cyclohexene mixtures (10, 20 and 30% of cyclohexene) in presence of a chromic oxide catalyst at 420-500°. They concluded that "irrespective of the composition of the original mixture, the olefin content of the catalyzate evidently tends to a definite limiting value, possibly to an equilibrium value; under the conditions studied the limit was at 6-8% of olefins in the mixture." Herington and Rideal [4] investigated the dehydrogenation of cyclohexane and mixtures of cyclohexane with cyclohexene (1, 2 and 3%) at 450°, and they also concluded that a stationary concentration of unsaturated hydrocarbons was established (1.65-1.73% in the catalyzate); the authors explained the constant concentration of unsaturated hydrocarbons in the catalyzates by kinetic factors; namely, by the ratio of the rates of dehydrogenation of cyclohexane to cyclohexene and of cyclohexene to benzene. Thermodynamic equilibrium cannot occur here: according to our calculations (based on the data of Korobov and Frost [19]), the equilibrium cyclohexane ⇌ cyclohexene + H_2 at 427-527° is displaced to the right by 89.6-98.7%.

On the other hand, it might be expected that the approximately constant concentration of unsaturated hydrocarbons in ethylcyclohexane dehydrogenation catalyzates could be the result of the existence of thermodynamic equilibrium in the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane:

ethylcyclohexane → ethylbenzene + $3H_2$ ⇌ styrene + $4H_2$

We have previously shown [13] that the constant styrene contents of ethylbenzene dehydrogenation catalyzates over a wide range of molar velocities result from the fact that this reaction attains a state of thermodynamic equilibrium. The identical relative increase in content of unsaturated products in catalyzates for identical dilution of ethylbenzene and ethylcyclohexane with carbon dioxide (see above) evidently results from the same cause: the inert diluent displaces the equilibrium in the direction of styrene. With the object of verifying the correctness of this hypothesis, the relevant thermodynamic calculation has been made.

SUMMARY

1. An investigation has been made of the high temperature dehydrogenation of ethylcyclohexane and ethylbenzene in presence of two catalysts at different temperatures (495° and 547°) and with and without a carbon dioxide diluent.

2. It has been found that the main products of the dehydrogenation of ethylcyclohexane are ethylbenzene and styrene. At the same time small amounts of unsaturated "by-products" are formed (probably ethylcyclohexene).

3. It has been shown that the ethylbenzene content of ethylcyclohexane catalyzates falls sharply as the molar velocity is increased, but the concentration of unsaturated products (mainly styrene) remains practically constant and is independent of the degree of aromatization of the ethylcyclohexane. The styrene content of the ethylbenzene dehydrogenation catalyzates also remains practically constant when the molar velocity is varied over a wide range, and it is several times as great as the concentration of unsaturated hydrocarbons in the ethylcyclohexane catalyzates.

4. It has been established, on the basis of these results, that the catalytic dehydrogenation of ethylcyclohexane proceeds in two stages: ethylcyclohexane → ethylbenzene → styrene.

5. It has been shown that identical dilution of ethylcyclohexane and ethylbenzene with carbon dioxide (a dilution of 2) leads to identical relative increase (by one third) in the content of unsaturated hydrocarbons in the catalyzates.

6. It has been suggested that the nondependence of the styrene content of ethylcyclohexane catalyzates on the degree of aromatization of the ethylcyclohexane results from the fact that the dehydrogenation of ethylbenzene, formed from ethylcyclohexane, attains a state of thermodynamic equilibrium.

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HIGH TEMPERATURE CATALYTIC DEHYDROGENATION OF ETHYLCYCLOHEXANE

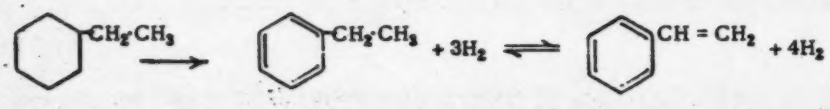
COMMUNICATION 2. THERMODYNAMIC EQUILIBRIUM IN THE DEHYDROGENATION OF ETHYLBENZENE UNDER THE CONDITIONS OF ITS FORMATION FROM ETHYLCYCLOHEXANE

I. I. Levitsky and N. I. Shuikin

The thermodynamic equilibrium ethylbenzene $\rightleftharpoons$ styrene + H_2, occurring under the conditions of formation of these substances from ethylcyclohexane, has been investigated by Herington and Rideal [1] at 500° in presence of an aluminum/chromium oxide catalyst. These authors found that the experimentally determined ratio styrene/ethylbenzene was twice as small as the value calculated from the constant K_E for the dehydrogenation of ethylbenzene. From these results the authors concluded that the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane does not attain a state of equilibrium, although, as was shown in the same investigation, the results for the dehydrogenation of pure ethylbenzene under the same conditions are in good agreement with theory. The authors used their results as a basis for the hypothesis that dehydrogenation of ethylcyclohexane to styrene proceeds through a series of intermediate stages (ethylcyclohexene, ethylcyclohexadiene, ethylbenzene) and the "competition" of ethylbenzene and the supposed intermediate substances for the catalyst surface retards the dehydrogenation of ethylbenzene and is the cause of the absence of equilibrium under these conditions.

We must point out, however, that the discrepancy, referred to above, between theoretical and experimental styrene/ethylbenzene ratios corresponds to an extremely small difference in the theoretical and experimental values of the yield of styrene from ethylcyclohexane: it is, for example, easy to calculate that for 60% aromatization of ethylcyclohexane at 500° (according to Herington and Rideal K_E = 0.0304) the difference is only 1.3%. The authors do not indicate what method they used for the determination of styrene in presence of other unsaturated hydrocarbons, although the probable error in the usual methods for the analysis of unsaturated hydrocarbons differs little from the difference stated above; consequently, inferences, based on such figures, concerning the absence of equilibrium and the mechanism of the reaction can scarcely be convincing.

In our previous communication [2] it was pointed out that the ethylbenzene content of catalyzates from the dehydrogenation of ethylcyclohexane falls sharply as the molar velocity increases, whereas the corresponding styrene content remains approximately constant, practically independent of the degree of aromatization of ethylcyclohexane. It was also found [3] that the dehydrogenation of pure ethylbenzene attains a state of thermodynamic equilibrium over a wide range of molar velocities. These results gave reason to suppose that, in the dehydrogenation of the ethylbenzene formed from ethylcyclohexane, a state of thermodynamic equilibrium was practically attained:



The first stage of this reaction is determined by kinetic factors: the equilibrium ethylcyclohexane $\rightleftharpoons$ ethylbenzene + $3H_2$ is displaced to the extent of 100% to the right even at 400° [4]. It is therefore clear that absolute equilibrium of the second stage is impossible owing to the continuous formation of ethylbenzene; for absolute equilibrium to be attained complete independence of the dehydrogenation of ethylbenzene of the time of contact would be necessary. In the present paper a thermodynamic calculation is made for the dehydrogenation

of ethylbenzene under the conditions of its formation from ethylcyclohexane, and a comparison is made between the theoretical and experimental results.

The calculation of equilibrium yields of styrene in the dehydrogenation of ethylcyclohexane is complicated by three supplementary factors*: a) the concentration of ethylbenzene is not constant, but changes with the degree of dehydrogenation of the ethylcyclohexane ring; b) the hydrogen formed by the dehydrogenation of the ethylcyclohexane ring displaces the equilibrium to the left; c) the original ethylcyclohexane, as a diluent for the components of the equilibrium mixture, displaces the equilibrium to the right.

These three factors, in their turn, depend on the degree of dehydrogenation of the ethylcyclohexane ring and so on the time of contact, activity of the catalyst, etc. These factors must be taken into account in a thermodynamic calculation of the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane:

$$\underset{4}{C_6H_{11}C_2H_5} = \underset{1}{C_6H_5C_2H_5} + \underset{3}{3H_2} = \underset{2}{C_6H_5CH{=}CH_2} + \underset{3}{4H_2}$$

When one mole of ethylcyclohexane is dehydrogenated with formation of x moles of ethylbenzene and the ethylbenzene formed is then dehydrogenated (to a state of equilibrium) with formation of y moles of styrene, the equilibrium mixture consists of:

Ethylbenzene	$n_1 = x - y$	moles
Styrene	$n_2 = y$	"
Hydrogen	$n_3 = 3x + y$	"
Ethylcyclohexane (inert diluent)	$n_4 = n_{in} = 1 - x$	"

By insertion of these expressions in the equation for the equilibrium constant for the dehydrogenation of ethylbenzene [3], we obtain:

$$K_E = \frac{n_2 n_3}{n_1(n_1 + n_2 + n_3 + n_{in})} = \frac{y(3x + y)}{(x - y)(1 + 3x + y)} \qquad (1)$$

and after rearrangement:

$$(1 + K_E)y^2 + (3x + 2K_E x + K_E)y - (K_E x + 3K_E x^2) = 0 \qquad (2)$$

The value of x in equation (2) corresponds to the sum of the yields of ethylbenzene and styrene from ethylcyclohexane ("degree of aromatization" of ethylcyclohexane). Knowing the value of the equilibrium constant K_E we may calculate the equilibrium yields of styrene y from ethylcyclohexane for various degrees of aromatization x of the latter.** This calculation has been performed for the temperature 547°. The equilibrium constant K_E calculated by the graphical method from the data in [5], which are computed from spectrum measurements, was found to be 0.0737 at 547°. The results of calculations of y from equation (2) ($K_E = 0.0737$) are presented in Table 1 and in the figure (upper curve). Complete dehydrogenation of ethylcyclohexane to ethylbenzene (or dehydrogenation of one mole of ethylbenzene in admixture with three moles of hydrogen) leads to an equilibrium yield of styrene of 8.9%. We may point out that the equilibrium degree of dehydrogenation of pure ethylbenzene to styrene for $K_E = 0.0737$ is 26.2%. Changes in the degree of aromatization of ethylcyclohexane are accompanied by extremely insignificant changes in the equilibrium yields of styrene: when the degree of aromatization of ethylcyclohexane is reduced by 20%, the

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*Supplementary to the usual factors: the value of K . the dilution, etc.

**The calculation of the theoretical yields of styrene from ethylcyclohexane may be performed also by another method, without taking the intermediate formation of ethylbenzene into account. When x moles of ethylbenzene and y moles of styrene are formed (by one or another route) from one mole of ethylcyclohexane, the mixture consists of: $n_1 = x$, $n_2 = y$, $n_3 = 3x + 4y$ and $n_{in} = 1 - (x + y)$. After insertion of these expressions in equation (1), we obtain:

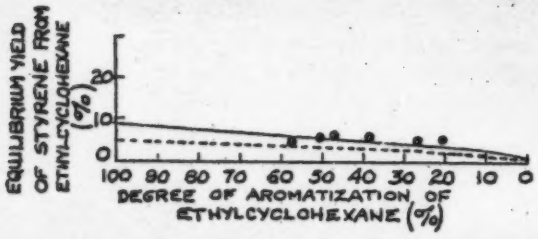
$$4y^2 + (3x - 4K_E x)y - (K_E x + 3K_E x^2) = 0. \qquad (3)$$

In equation (3) the value of x corresponds to the yield of ethylbenzene from ethylcyclohexane. Calculations of theoretical yields of styrene from equations (2) and (3) yield identical results.

TABLE 1

Equilibrium Yields of Styrene from Ethylcyclohexane at 547° for Different Degrees of Aromatization of the Latter (K_E = 0.0737)

Degree of aromatization of ethylcyclohexane (%)	Equilibrium yields of styrene from ethylcyclohexane (%)
100	8.9
80	7.5
60	6.1
40	4.7
20	3.2


EQUILIBRIUM YIELD OF STYRENE FROM ETHYLCYCLOHEXANE (%)
20
10
0
100 90 80 70 60 50 40 30 20 10 0
DEGREE OF AROMATIZATION OF ETHYLCYCLOHEXANE (%)

Equilibrium yields of styrene from ethylcyclohexane at 547° for various degrees of aromatization of the latter. The upper curve is calculated for K_E = 0.0737, computed from spectrum data. The lower curve is calculated for K_E = 0.0374, computed from experimental data. ● – experiments on the dehydrogenation of ethylcyclohexane over V_2O_5-Al_2O_3.

equilibrium yield of styrene falls by only 1.4%. These results can supply the explanation of the approximate constancy, noted above, in the styrene content of ethylcyclohexane dehydrogenation catalyzates over a wide range of degree of aromatization.

A comparison of the calculated and experimental yields of styrene from ethylcyclohexane was made on the basis of the results given in Table 4 of our previous communication [2]. These results refer to a series of experiments in which ethylcyclohexane and ethylbenzene were dehydrogenated in absence of diluent at 547° in presence of an aluminum/vanadium oxide catalyst.

It was shown in the same paper that the unsaturated hydrocarbons in the united catalyzate from this series contained 65% of styrene. From this value, the yields of catalyzates, and results of the bromometric determination of unsaturated hydrocarbons, the yields of styrene, based on the ethylcyclohexane passed, were calculated for the separate experiments. Also, on the basis of the degree of aromatization of ethylcyclohexane and the value of K_E = 0.0737 the theoretical yields of styrene from ethylcyclohexane were calculated. The results of these calculations are given in Table 2. A comparison of the theoretical and experimental yields of styrene is shown in the graph. The difference in theoretical and experimental yields (see column 11, Table 2) does not exceed 1.3%, which is

TABLE 2

Dehydrogenation of Ethylcyclohexane without Diluent at 547° in Presence of an Aluminum/Vanadium Oxide Catalyst

Expt. No.	Molar rate of passage of ethylcyclohexane (mole/l. liter-hr)	Yield, on ethylcyclohexane passed, of catalyzate (%)	Content of reaction products in catalyzate (%)		Yield, on ethylcyclohexane passed, of reaction products (%)		Degree of aromatization of ethylcyclohexane (%) *	Yield, on ethylcyclohexane passed, of styrene (%)	Theoretical yield of styrene from ethylcyclohexane (%)	Discrepancy (%)
			Ethylbenzene	Unsaturated hydrocarbon	Ethylbenzene	Unsaturated hydrocarbon				
1	2	3	4	5	6	7	8	9	10	11
99	0.7	67	78.6	10.4	52.7	7.0	57.3	4.6	5.9	−1.3
98	2.0	77	58.9	11.1	45.4	8.5	50.9	5.5	5.5	0
100	3.1	85	49.6	9.9	42.2	8.4	47.7	5.5	5.2	+0.3
101	4.0	83	40.6	9.9	33.7	8.2	39.0	5.3	4.6	+0.7
133	6.3	93	23.6	8.0	21.9	7.4	26.7	4.8	3.7	+1.1
134	11.7	92	17.4	7.3	16.0	6.7	20.4	4.4	3.2	+1.2

*The degree of aromatization of ethylcyclohexane was obtained by adding the values in columns 6 and 9.

close to the probable error of the analytical method used. These results show that the reaction under consideration has practically attained a state of thermodynamic equilibrium.

In our investigation [3] of the part played by inert diluents in the catalytic dehydrogenation of ethylbenzene, it was shown that the results of experiments on the dilution of ethylbenzene with nitrogen and toluene were in good agreement with calculations from the experimental equilibrium constant. It was of interest to calculate the yields of styrene from ethylcyclohexane on the basis of a value of K_E calculated from experimental quantities. In Table 4 of the previous communication [2] results were given of ethylbenzene dehydrogenation experiments that alternated with the ethylcyclohexane dehydrogenation experiments considered above. In these experiments the average yield of styrene was 19.0% on the ethylbenzene passed, and the corresponding value of K_E is 0.0374. The results of calculations, on the basis of $K_E = 0.0374$, of the yields of styrene from ethylcyclohexane are given by the lower graph in the figure. The yields of styrene calculated in this way are 2.5-2.8% less (except Expt. 99) than the experimental values obtained in the dehydrogenation of ethylcyclohexane. It should be remembered that discrepancies of a similar nature were observed by us [3] also in the dehydrogenation of ethylbenzene in admixture with hydrogen: the experimental yields of styrene were 3-4% greater than those calculated from the experimental K_E It is probable that these discrepancies have the same cause. The low concentrations of styrene in the catalyzates both of ethylcyclohexane and of ethylbenzene when diluted with hydrogen caused a lower degree of polymerization than that occurring in experiments with pure ethylbenzene, on the results of which the calculation of the experimental K_E is based.

From the present investigation it follows that the low yields of styrene from ethylcyclohexane are the result of the presence of thermodynamic equilibrium between ethylbenzene, styrene, and hydrogen, as formed from ethylcyclohexane. It is interesting to note that the thermodydnamic equilibrium ethylcyclohexane $\rightleftharpoons$ styrene $+ 4H_2$ is almost completely displaced on the side of styrene at 500-600°. The effecting of this reaction demands the direct dehydrogenation of ethylcyclohexane to styrene without the intermediate or subsequent formation of ethylbenzene. Such a reaction, however, is impossible: it is scarcely possible for there to be a catalyst that will initiate the dehydrogenation of ethylcyclohexane to styrene, but cannot hydrogenate styrene to ethylbenzene.

SUMMARY

1. A thermodynamic calculation has been performed for the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane at 547°. Equilibrium yields of styrene from ethylcyclohexane change by only 1.4% when the degree of aromatization of ethylcyclohexane changes by 20%.

2. It has been shown that the experimental yields of styrene from ethylcyclohexane coincide (within the limits of the accuracy of the analysis) with theoretical figures. Hence, the dehydrogenation of ethylbenzene formed from ethylcyclohexane attains equilibrium.

3. It has been established that the nondependence of the yields of the final product of the dehydrogenation of ethylcyclohexane (styrene) on changes over a wide range in the progress of the intermediate stage of this reaction (yield of ethylbenzene) results from the fact that the dehydrogenation of ethylbenzene formed from ethylcyclohexane attains an equilibrium.

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* See Consultants Bureau Translation, page 895.

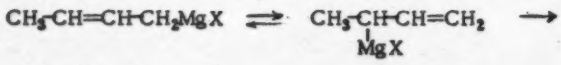
** See Consultants Bureau Translation, page 599.

*** See Consultants Bureau Translation, page 365.

REACTION OF THE GRIGNARD REAGENT FROM 3-CHLORO-2,4-DIMETHYL-1-PENTENE WITH 2,4-DIMETHYL-3-PENTANONE, ETHYL FORMATE, AND AMYL BUTYRATE

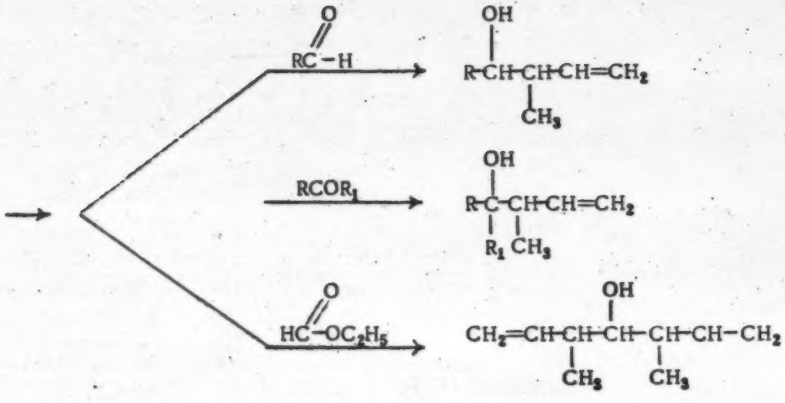
V. A. Ponomarenko and T. Ya. Tolkacheva

The investigations of Young and Roberts with coworkers [1-5] and Ou Kiun Houo [6] have revealed an extremely interesting example of the allyl rearrangement; namely, the tendency for the reaction of 2-butenylmagnesium halide with a number of carbonyl compounds* to yield alcohols corresponding to the secondary form of the Grignard reagent (II):



(I) (II)

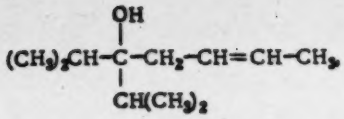
Primary form Secondary form



where X = Br, Cl.

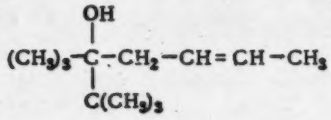
It should be noted that it is immaterial as regards the result of the process whether we take pure isomeric halobutenes for the reaction ($CH_3-CH=CH-CH_2X$ or $CH_3-\underset{X}{CH}-CH=CH_2$), or the mixture of these that is readily formed as a result of the allyl rearrangement $CH_3-CH=CH-CH_2X \rightleftharpoons CH_3-\underset{X}{CH}-CH=CH_2$. Among the carbonyl compounds that have been studied in connection with this reaction are the following: formaldehyde [2,10], acetaldehyde [2,6,7], propionaldehyde [6,7], acrolein [6,7], benzaldehyde [7], acetone [2], 2,4-dimethyl-3-pentanone [3], 2,2,4-trimethyl-3-pentanone [4], 2,2,4,4-tetramethyl-3-pentanone [4], 2',4',6'-trimethylacetophenone [5], 2',4',6'-trimethylisobutyrophenone [4], benzophenone [4], and ethyl formate [9]. In reactions with ketones, steric hindrance effects are found; in the case of 2,4-dimethyl-3-pentanone [3], it is manifested by the simultaneous formation of the isomeric alcohol

*A similar tendency is shown in the reactions of 2-butenylmagnesium halide with CO_2 [1,2], ethyl orthoformate [9,10], and phenyl isocyanate [9].



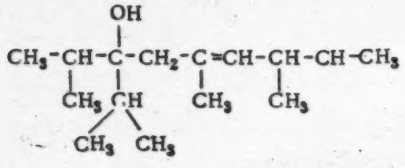
corresponding to the primary form of the Grignard reagent (I) (15% for 2-butenylmagnesium bromide and 6% for 2-butenylmagnesium chloride).*

2,2,4,4-Tetramethyl-3-pentanone; i.e., a ketone in which pronounced steric hindrance occurs, forms only the alcohol corresponding to the primary form of the reagent, 2-butenylmagnesium halide (I):

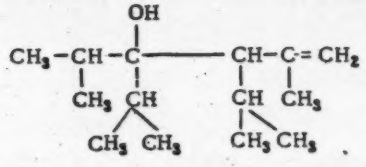


We considered it to be of interest to study the reaction of considerably more "sterically hindered" unsaturated Grignard reagents prepared from 3-chloro-2,4-dimethyl-1-pentene with 2,4-dimethyl-3-pentanone and determine: 1) the possibility, in general, of forming a tertiary alcohol, it being known that saturated, less "sterically hindered," secondary alkylmagnesium halides** do not form the corresponding tertiary alcohols, but merely reduce the 2,4-dimethyl-3-pentanone to 2,4-dimethyl-3-pentanol, and 2) the effect on the course of the reaction of greater steric hindrance in our alkenylmagnesium halide (than in 2-butenylmagnesium halide), if a tertiary alcohol is formed.

It was found that the Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene reacts fairly readily with 2,4-dimethyl-3-pentanone, yielding an alcohol of composition $C_{14}H_{27}OH$ in 40% yield. Ozonization of this alcohol gave the following results: the main products isolated were isobutyric acid (via the amide) and an unsaturated ketone of composition $C_{10}H_{18}O$; it was shown that formic acid was present in traces. Hence, of the two alcohols that are possible in this case:



(III)

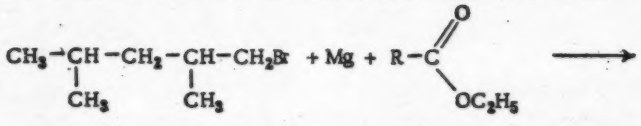


(IV)

the main reaction product was (III). On being ozonized, it gave isobutyric acid and a hydroxy ketone, which lost a molecule of water and was converted into the unsaturated ketone $C_{10}H_{18}O$. This ketone gave a semicarbazone of m.p. 195°.

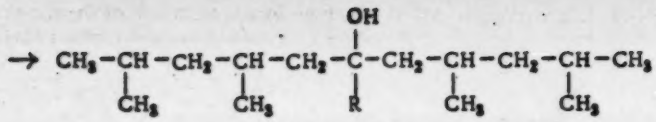
The presence in the ozonization products of formic acid evidently indicates the presence of a small amount of the alcohol (IV) in the reaction products. We were unable, however, to isolate the corresponding ketone. In its reaction, therefore, with 2,4-dimethyl-3-pentanone the Grignard reagent from 3-chloro-2,4-dimethyl-1-pentane behaves in an essentially different manner from 2-butenylmagnesium chloride, the explanation evidently lying in the greater steric hindrance that is present.

In 1947 Tuot and Guyard [8], who were trying to prepare certain branched hydrocarbons having 15 and 16 carbon atoms, were unable to obtain the alcohols required as starting materials by the reactions:

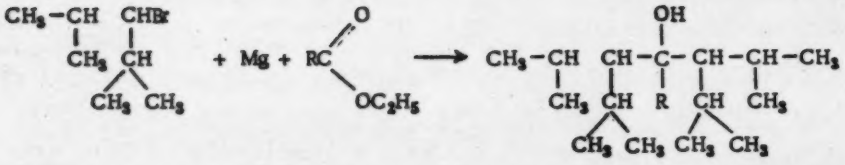


*The remaining 85% and 94% respectively is to be assigned to alcohol formed from the secondary form of the Grignard reagent (II). The total yield of alcohols is 84-89%.

**These include isopropylmagnesium bromide and sec-butylmagnesium bromide.



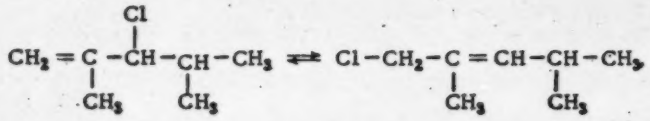
(1)



(2)

where R = CH_3, H. Tuot and Guyard explained their lack of success by the presence in the alkyl halides of steric hindrance, which resulted in side reactions: formation of 2,4-dimethylpentane, 2,4-dimethyl-1-pentene, 2,4-dimethyl-2-pentene, 3,5-dimethyl-1-hexanol, and 2-isopropyl-3-methyl-1-butanol.

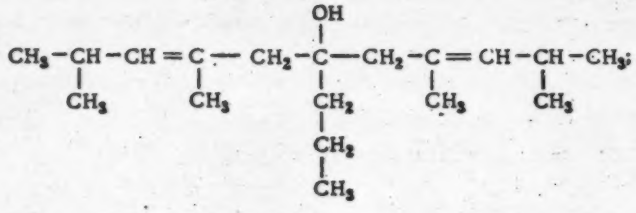
We did not undertake the task of studying the structure of the alcohols obtained by reaction of the Grignard reagent from 3-chloro-2,4-dimethyl-1-pentene with ethyl formate and with amyl butyrate; we attempted only to establish the nature of the effect on the course of the synthesis of the double bond in the β-position in the allyl rearrangement system from 3-chloro-2,4-dimethyl-1-pentene:

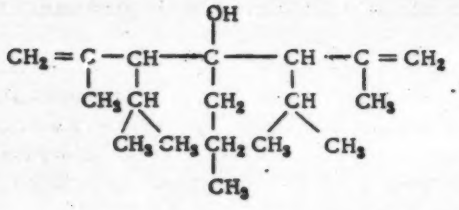


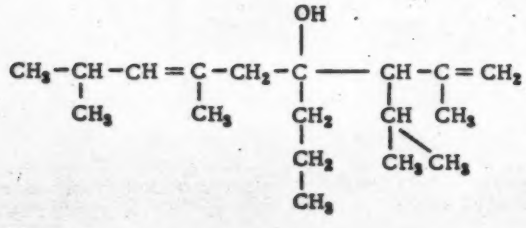
the structural analog of Tuot and Guyard's bromides.

Reaction with ethyl formate yielded the formic ester of an alcohol $C_{15}H_{27}OH$ in 23% yield; it was readily hydrolyzed, yielding the alcohol $C_{15}H_{27}OH$. With amyl butyrate the yield of alcohol attained 36%.

It is of interest that in this case no ester was formed. Ozonization of this alcohol gave formic and isobutyric acids. As we did not analyze the neutral products, we were unable to assign the alcohol any particular one of the three possible structures:







It is possible that the alcohol $C_{18}H_{33}OH$ is a mixture of all of the three forms, with one of them predominating. In spite of the complex picture presented, the fact of the favorable effect of a double bond β to the halogen on the course of the synthesis of highly branched alcohols is worthy of attention.

EXPERIMENTAL

3-Chloro-2,4-dimethyl-1-pentene

3-Chloro-2,4-dimethyl-1-pentene was prepared by the chlorination of 2,4-dimethyl-2-pentene (b.p. 81-82.5°; n_D^{20} 1.4035; d_4^{20} 0.6948). From 189 g of 2,4-dimethyl-2-pentene in three experiments 98 g of 3-chloro-2,4-dimethyl-1-pentene was obtained. After two distillations at 30 mm Hg, the chloro compound had b.p. 40-42.5°, n_D^{20} 1.4393; d_4^{20} 0.8944. The structure of this chloro compound has been proved by us in a previous communication [11].

Reaction of the Grignard Reagent from 3-Chloro-2,4-dimethyl-1-pentene with 2,4-Dimethyl-3-pentanone.

Dry 2,4-dimethyl-3-pentanone (17.2 g; b.p. 123°, n_D^{20} 1.4010) was added to iso-$C_7H_{13}MgCl$ prepared from 25 g of 3-chloro-2,4-dimethyl-1-pentene and 9.2 g of magnesium in 150 ml of absolute ether with vigorous mixing and very slow addition of the chloro compound. The reaction mixture was heated for four hours and then decomposed with 150 ml of ice water. The ether layer was separated and dried over calcined $CuSO_4$. After removal of ether and vacuum fractionation, 13.8 g of an alcohol was obtained. The reaction was repeated, 40.6 g of alcohol being obtained altogether.

A further fractionation at 3.5 mm yielded the following fractions:

Fraction I, b.p. up to 78.5°; 6.3 g; n_D^{20} 1.4595; d_4^{20} 0.8524
Fraction II, b.p. 78.5-80.5°; 30.5 g; n_D^{20} 1.4620; d_4^{20} 0.8614

Found MR 67.78
Calculated MR 67.91

$C_{14}H_{27}OH$. Found %: C 78.97; 78.82; H 13.21; 13.25
Calculated %: C 79.18 H 13.29

Ozonization of the Alcohol $C_{14}H_{27}OH$

A solution of 10 g of the alcohol in 55 ml of dry chloroform was ozonized with 4% ozone (6 liters per hour) for 15 hours. The ozonide was decomposed with 60 ml of 3% H_2O_2 with vigorous stirring, at first at room temperature, and then in a water bath for eight hours. The acids were neutralized with sodium carbonate. The aqueous layer was evaporated to dryness. The salts of the acids were decomposed with 20 ml of 20% H_2SO_4. The acids were extracted with ether and dried over calcined Na_2SO_4. The ether was driven off, and the acids were distilled at atmospheric pressure, yielding the fractions:

Fraction I, b.p. 97-138°; 0.55 g; n_D^{23} 1.3816
Fraction II, b.p. 138-150°; 1.0 g; n_D^{22} 1.3901

The residue was a small amount of resin. A content of 31 mg of formic acid was found in Fraction I by the calomel method. Fraction II was treated with 1.5 g of thionyl chloride at 90-95° for 30 minutes. The acid chloride was carefully introduced into 20 ml of 27% ammonia solution at −10°. Water was evaporated away at room temperature. A part of the solid residue was vacuum-sublimated: the melting point of the amide so obtained was 125-126°, that of the amide of authentic isobutyric acid was 127-128°, and that of a mixture of these preparations was 125-127°. The chloroform layer and the ether extracts from the aqueous layer after it had been treated with sodium carbonate were united and dried over calcined Na_2SO_4. The ether and chloroform were distilled off under atmospheric pressure, and the residue distilled under reduced pressure (4 mm), yielding the fractions:

Fraction I, b.p. up to 67°; 4.4 g; n_D^{21} 1.4494
Fraction II, b.p. 67-84°; 0.5 g; n_D^{21} 1.4525
Fraction III, b.p. 84-90°; 0.5 g; n_D^{21} 1.4614
Fraction IV, b.p. above 90° — a resin

Fraction I was redistilled at 8 mm Hg:

Fraction I, b.p. 57-60°; 2.2 g; n_D^{20} 1.4474; d_4^{20} 0.8618
Fraction II, b.p. 60-63°; 1.9 g; n_D^{20} 1.4505

MR for fraction of b.p. 57-60°: found 47.86, calculated for $C_{10}H_{18}O$, 47.95.

From the same fraction a semicarbazone was prepared; after two crystallizations from ethanol it melted at 195°.

	Found %:	C 63.10; 63.09;	H 10.05; 9.85; N 20.37; 20.63
$C_{11}H_{21}N_3O$.	Calculated %:	C 62.52	H 10.02 N 19.89

Fraction III of the first fractionation, in which the ketone $C_{13}H_{26}O_2$ corresponding to the alcohol (IV) might be supposed to occur, gave an insignificant amount of semicarbazone, m.p. 192° (single crystallization from alcohol); its melting point in admixture with the semicarbazone from Fraction I was 192-193.5°.

Dehydration of the Alcohol $C_{14}H_{27}OH$

The alcohol (20.3 g) was mixed with 3 g of anhydrous $CuSO_4$ and heated for several hours at 150°, yielding 14 g of a diolefin, b.p. 76-78° (8 mm); d_4^{20} 0.7910; n_D^{20} 1.4527.

The diolefin was hydrogenated, first over platinized charcoal in presence of chloroplatinic acid, and then in an autoclave over nickel at 190-230° and 200-230 atm. The product, after the usual treatment and distillation over sodium, was 2,5,7-trimethyl-3-isopropyloctane, which has been previously synthesized by Petrov and Ponomarenko [11] by another method.*

Reaction of i-$C_7H_{13}MgCl$ with Amyl Butyrate

A solution of amyl butyrate (21 g) in 50 ml of absolute ether was added dropwise with stirring to i-$C_7H_{13}MgCl$ prepared from 35.5 g 3-chloro-2,4-dimethyl-1-pentene and 6.45 g of magnesium in 100 ml of absolute ether. The reaction mixture was heated for six hours in a water bath and was then decomposed with ice water. The ether solution of the reaction products, together with ether extracts, was dried over anhydrous Na_2SO_4. The ether was distilled off and the residue vacuum-fractionated, yielding 12.6 g (35.5%) of an alcohol, b.p. 142-144°/11 mm; d_4^{20} 0.8659; n_D^{20} 1.4712; calculated MR 85.92; found MR 86.04.

	Found %:	C 81.32; 81.34;	H 12.71; 12.82
$C_{18}H_{35}OH$.	Calculated %:	C 81.13;	H 12.86

Ozonization of the Alcohol $C_{18}H_{35}OH$

A solution of 8.8 g of the alcohol in 40 ml of dry chloroform was ozonized with 6% ozone (4 liters per hour) for 12 hours. The ozonide, in its chloroform solution, was then decomposed by treatment, accompanied by vigorous stirring, with 100 ml of 1% H_2O_2 for six hours at room temperature and six hours in a water bath. A further 4 ml of 25% H_2O_2 was then added, and the decomposition products were heated in a water bath for one hour further. The acids were neutralized with sodium carbonate, and the neutral products were extracted with ether. Analysis by the calomel method revealed the presence of 0.364 g of formic acid.

The neutral solution of salts was evaporated down, and the salts were decomposed with 20% H_2SO_4. The acids were extracted with ether, and the ether extracts were dried over anhydrous Na_2SO_4. The ether was distilled off, and the residue (0.6 g) treated with 1.5 g of thionyl chloride for 30 minutes at 90-95°, and then with a 22% solution of ammonia. The product was 70 mg of amide, which after several sublimations and drying over calcined $CaCl_2$ melted at 121-123°. The melting point of the amide of authentic isobutyric acid was 125-126°, and the mixed melting point was 124-125°. The neutral products were not analyzed.

Reaction of i-$C_7H_{13}MgCl$ with Ethyl Formate

Dry ethyl formate (9.8 g) was added slowly (dropwise) to i-$C_7H_{13}MgCl$ prepared from 35.5 g of 3-chloro-2,4-dimethyl-1-pentene and 6.45 g of magnesium in 120 ml of absolute ether. The temperature of the reaction mixture was maintained at about +5°. The mixture was set aside for 30 hours, and a further 45 ml of dry ether was then added. The mixture was then heated for five hours, decomposition was effected with ice water, and the reaction products were extracted with ether. The ether extract was dried, and the ether was distilled off. The residue was distilled twice at 3 mm in a current of nitrogen, yielding 7.3 g (23%) of the formic ester of an alcohol of composition $C_{15}H_{27}OH$; b.p. 111-113° (3 mm); d_4^{20} 0.9099; n_D^{20} 1.4662; found MR 76.85; calculated MR 76.81.

	Found %:	C 76.04; 75.95;	H 11.21; 11.18
$C_{16}H_{28}O_2$.	Calculated %:	C 76.14	H 11.18

* We take the opportunity of correcting one of the constants of this hydrocarbon: n_D^{20} 1.4370, and not 1.4310 as stated.

Hydrolysis of the Ester $C_{16}H_{28}O_2$.

The ester was hydrolyzed with 11 g of KOH in 50 ml of methanol. The mixture was boiled in a water bath for 12 hours, and the hydrolysis mixture then mixed with a large amount of water. The upper layer was extracted with ether, and the ether was removed from the extract. The product was 3.2 g of an alcohol, b.p. 111-113° (9 mm); d_4^{20} 0.8719; n_D^{20} 1.4670; found MR 71.40; calculated MR 72.06.

	Found %:	C 80.09; 80.04;	H 12.76; 12.52
$C_{15}H_{27}OH$	Calculated %:	C 80.29;	H 12.57

SUMMARY

1. The reactions of the Grignard reagent derived from the "sterically hindered" 3-chloro-2,4-dimethyl-1-pentene with 2,4-dimethyl-3-pentanone, ethyl formate, and amyl butyrate indicate the favorable effect of a double bond in the β-position on the synthesis of highly branched alcohols, which cannot be prepared by reaction with the corresponding saturated haloalkanes.

2. It has been shown that the Grignard reagent derived from 3-chloro-2,4-dimethyl-1-pentene differs fundamentally from 2-butenylmagnesium chloride in that its reaction with 2,4-dimethyl-3-pentanone gives as its main product the alcohol corresponding to the primary form of the alkenylmagnesium halide.

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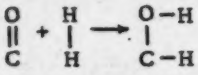
SEMICATALYTIC HYDROGENATION AND DEHYDRATIONAL CONDENSATION IN THE MECHANISM OF THE ISO SYNTHESIS

Ya. T. Eidus

The synthesis of hydrocarbons from carbon monoxide and hydrogen at normal or medium (10-15 atm) pressures is effected in presence of catalysts containing metals of Group VIII of the periodic system. The mechanism of the synthesis is most probably as follows [1]. Carbon monoxide and hydrogen molecules are activated at the catalyst surface and yield the unstable active group CHOH, formed in the first hydrogenation step from a CO molecule and an H_2 molecule. In the second hydrogenation step at the surface, the group CHOH reacts with a new H_2 molecule, forming a water molecule and a methylene group attached to the catalyst surface [2]:



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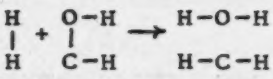
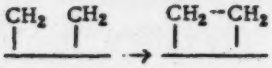


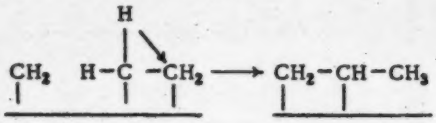
(2)

This is succeeded by polymerization of methylene radicals at the surface of the catalyst. This process proceeds so that at first two methylene radicals combine to give an ethylene molecule adsorbed on two catalyst centers:



(3)

A new methylene group then unites to one of the two carbon atoms of the ethylene, and simultaneously an atom of hydrogen migrates and a methyl group is formed. As a result a molecule of propene is formed, and this also is attached to the catalyst surface at two centers.



(4)

The process is continually repeated with the successive formation of molecules of butene, pentene, etc., also held on the surface by two atoms.

This mechanism of methylene radical polymerization is confirmed by the reaction of hydrocondensation of carbon monoxide with the simplest olefins [3]. Under certain conditions of synthesis, e.g., on iron catalysts, the water separating in the reaction of equation (2) participates in the water-gas reaction:

$$CO + H_2O \rightleftharpoons H_2 + CO_2, \qquad (5)$$

and one of the final reaction products is, therefore, CO_2 [4]. It follows from the above discussion that the catalyst used in the synthesis has at least two functions: 1) to hydrogenate, and 2) to polymerize.

It is fairly often suggested in the literature that the fulfilling of the separate functions of a catalyst that is effecting a complex reaction is to be attributed to separate components of the catalyst [5]. Such differentiation of the action of catalyst with respect to its components is generally based on the properties of the isolated components. Such a point of view does not correspond altogether accurately to the actual state of affairs, inasmuch as the catalyst acts in all cases as a single whole and all qualitative and quantitative changes in its composition

always affect all its functions in greater or less degree [6], but the notion nevertheless contains a certain amount of truth and enables us to consider the question of the effect of separate components of the catalyst on its various properties. Actually, separate functions of a catalyst can be strengthened or weakened, or even completely removed, while others are preserved. The addition, for example, of an alkaline agent increases the polymerizing action of a catalyst, and, as a result, the yield of high boiling fractions and solid paraffin is raised [5]. The hydrogenating propensity rises as we pass from iron catalysts to cobalt and further to nickel. Correspondingly, the content of unsaturated hydrocarbons in the gasoline fraction, b.p. up to 150°, falls from 80% to 31% and further to 12% [7]. These data show that the hydrogenating properties of the catalyst can be attributed to its main component, a metal of Group VIII. Similarly, the polymerizing effect is to be ascribed to difficultly reducible oxides: ThO_2, MnO, MgO, Al_2O_3, and others, which are present in the catalyst in small amount. To some of these, such as ThO_2 and Al_2O_3, a dehydrating effect is also ascribed, and this aids the elimination of water in the formation of CH_2 radicals [8].

The hydrogenating ability of a catalyst may be evaluated by carrying out the hydrogenation of olefin or aromatic hydrocarbons in its presence [6]. It follows from the above discussion that the hydrogenating component is essential for a synthesis catalyst. Until recently the only catalysts known for the practical synthesis of hydrocarbons from carbon monoxide and hydrogen contained Group VIII metals, Ni, Co, Fe, and Ru. Recently, however, the synthesis has been effected of hydrocarbons that are predominantly of the iso structure (iso synthesis) from carbon monoxide and hydrogen in presence of catalysts that do not contain any Group VIII metals, but consist only of zinc oxide or of difficultly reducible metal oxides, such as thorium, aluminum, and cerium oxides, taken separately or in pairs [9,5]. As an additive, an alkaline agent may be used [9,5]. The iso synthesis proceeds under the following optimum conditions: 450° at 300-600 atm; initial mixture approximately 1 CO : 1 H_2; space velocity for the passage of the mixture 500-1000 liters per liter of catalyst per hour. On ThO_2 at 450° and 600 atm the yield of products is 154 g per cubic meter; they include 18.2% of $CH_4 + C_2H_6$; 14.7% $C_3H_8 + n\text{-}C_4H_{10}$; 3.3% $(CH_3)_2O$; 29.3% of isobutane and isobutene, and 34.5% of liquid products.

On the catalyst ThO_2–Al_2O_3 the yield of liquid products is 56 g per cubic meter, and the C_4 fraction amounts to 61 g per cubic meter. The latter contains 80-90% of hydrocarbons of iso structure. At pressures of more than 600 atm and temperatures below 400° a considerable amount of oxygen compounds is obtained; it consists mainly of methyl and isobutyl alcohols and dimethyl ether.

In the liquid product obtained at 450° and 300 atm [10], the C_5 fraction varies, according to the catalyst, from 5 to 27%, the C_6 fraction from 12 to 28%, and the C_7 fraction from 15 to 22%. The content of normal hydrocarbons is low. After hydrogenation of the product, the n-pentane content of the C_5 fraction is 11-19%; in the C_6 fraction the n-hexane content does not exceed 3-5.5%, whereas the 2-methylpentane content is 28-59%, the 2,3-dimethylbutane content is 11-41%, and the 3-methylpentane content is 10-16%; in the C_7 fraction, the sum of the amounts of 2- and 3-methylhexanes and 2,3-dimethylpentane comprises 28-44% of the fraction. In the iso synthesis, hydrocarbons having a tertiary carbon are also formed, although in small amounts. In the C_6 fraction 0.6-3.4% of neo-hexane is present, and in the C_7 fraction there is 0.4-12% of 2,2-dimethylpentane, and the greatest amount of such hydrocarbons is formed in presence of catalysts containing aluminum oxide. Products of the iso synthesis include also cycloalkanes: up to 1.2% of the C_5 fraction is cyclopentane, 2-15% of the C_6 fraction is methylcyclopentane, and the C_7 fraction contains 3-10% of methylcyclohexanes and 9-29% of dimethylcyclopentanes. The C_6 fraction contains also cyclohexane.

Two features of the iso synthesis deserve special attention from the theoretical point of view. First, the occurrence of the process in presence of catalysts that do not possess hydrogenation properties (Al_2O_3, ThO_2); second, the formation of hydrocarbons of iso structure. Let us examine these two peculiarities of the iso synthesis more closely and try to establish some relationship between them.

According to the most widely accepted modern theories of heterogeneous catalysis, particularly the multiplet theory [11], catalytic reactions proceed in the adsorbed layer. First of all, all the initial components of the reaction are activated when they are adsorbed on the surface; this may be expressed for the reaction

$$A + B \rightarrow C \qquad (6)$$

$$A + B \rightarrow \underline{\overset{A}{\vdots}\ \overset{B}{\vdots}} \rightarrow \underline{\overset{A}{\vdots}\cdots\overset{B}{\vdots}} \rightarrow \underline{\ \ C\ \ } \qquad (7)$$

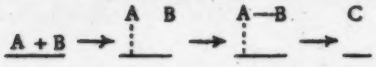
Consequently, the hydrogenating ability of a catalyst with respect, for example, to olefins is conditioned in the first place by its having the property of activating hydrogen molecules, as well as olefins molecules, when they come into contact with the surface. The absence of such hydrogenating ability may result from the impossibility of the activation of hydrogen molecules, or of olefin molecules, or of both simultaneously. It is well known that aluminum oxide is active in the reactions of the simplest olefins – for example, in hydration reactions.

It may be assumed, however, with great confidence, that aluminum oxide and other such dehydrating catalysts for the iso synthesis are unable to activate hydrogen molecules; carbon monoxide molecules, on the contrary, are activated by these catalysts, a fact proved beyond doubt by the occurrence, under the conditions of the synthesis, of the Boudouard-Bell reaction [5].*

We may conclude from this discussion that in the iso synthesis in presence of Al_2O_3, ThO_2, and other catalysts the reaction proceeds without preliminary activation of hydrogen molecules by the catalyst, although it undoubtedly proceeds with the participation of hydrogen molecules. Hence, in spite of the demands made by the theories referred to above [11], a catalytic reaction may proceed in certain special cases without the activation on the catalyst of certain** of the initial components, which may therefore react with their partners on the catalyst without being in the adsorbed condition themselves. For the reaction of equation (6), this can be expressed by

(8)

or



(9)

The activation of such reaction components is, of course, of a purely thermal character. There are only a few references in the literature [12-15] to the possibility of the occurrence of hydrogenation in this way in other reactions. It was shown, however, in a study of the reactions of hydrogen containing deuterium in presence of catalytically active nickel [14] that at 20° and at 10 mm Hg the participation of ethylene in the reaction completely inhibited the para—ortho transformation of hydrogen, although hydrogenation occurred at zero order with respect to ethylene. The explanation advanced was that the nickel surface was, under these conditions, completely covered with ethylene, which prevented the adsorption and para—ortho transformation of hydrogen, but which was able to unite with hydrogen, possibly without the preliminary dissociation of this into atoms in the adsorbed layer.

Under the conditions of iso synthesis, the activation of hydrogen by the catalyst is evidently prevented not by the complete covering of the catalyst surface by carbon monoxide, but by the nature of the catalyst itself, and also, possibly, by the high temperature of the process. In this way there arises the idea of the possibility of the existence, in special cases, of "semicatalytic" reactions, which have as yet received very little study; the characteristic feature of such reactions is that some of the original reactants are activated by contact with the surface and remain bound to it during the reaction, and other reactants, on the contrary, are activated only thermally and may be in the gas phase during the reaction, although they will react with their reaction partners, which are attached to the catalyst.

According to the multiplet theory [11], in catalytic reactions only those atoms of the reactant molecules react that are directly bound to the catalyst surface. The reactant molecule must touch at least two active atoms of the surface, since the rupture of old, and formation of new, chemical bonds occurs between atoms that are attracted by different active atoms of the catalyst. The reaction center, therefore, coincides with a catalyst site. It is clear that, for the occurrence of a "semicatalytic" reaction, it is quite sufficient for the activated component attached to the catalyst to be linked to only one active atom of the surface.

Such activation of a molecule by contact with one active center does not always fix the place of reaction on the catalyst surface. Reaction with a molecule from the gas phase may occur both at the atom attached to the surface, and also with the atom not directly attached to the surface In the latter case, the activation of the molecule attached to the catalyst through its bond with an atom of the catalyst and the effect of the latter on various atoms of the molecule attached to the catalyst find an analogy in that which in the chemistry of molecules is called "the mutual effect of atoms not directly linked together" [16]. Activation by contact therefore implies, not only molecular deformation and dynamic tension [17], but also the effect of the catalyst on the reactivity of atoms in the molecule attached to the catalyst. These two aspects are not in conflict, but are different manifestations of the same actuality—activation by contact. In a certain sense, Mendeleev was considering

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*The carbon formed by this reaction ($2CO \rightleftharpoons C + CO_2$) cannot initiate a hydrogenating function [17].

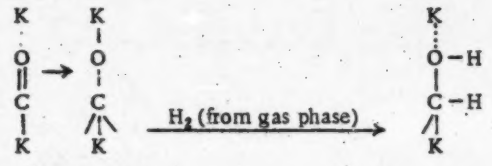
** But not all; otherwise the reaction would be not catalytic, but thermal.

the chemical nature of interaction during catalysis when he wrote: "The degree, and even the period, of the perturbations or changes in movement will depend on the individual characters of the bodies coming into contact; ie., will have a purely chemical character" [18].

"Semicatalysis" occupies an intermediate place between heterogeneous catalysis and homogeneous thermal reaction, inasmuch as the molecules of one reactant are activated by the catalyst, and the molecules of the other are activated thermally. It follows that semicatalytic reactions of this kind play an increasing part as the temperature of the chemical process rises, while not exceeding the temperature of the thermal reactions. Since the purely heterogeneous reaction goes, as is well known, with a lower activation energy than the corresponding thermal reaction, the activation energy for a semicatalytic reaction must be higher than for a purely heterogeneous reaction, but lower than for a thermal reaction.

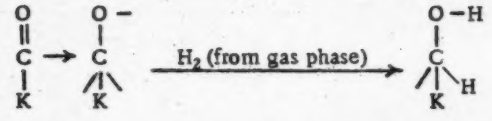
"Semicatalysis," as an intermediate form, is essentially distinct from other known transitional forms, such as catalysis in films on the surface of a heterogeneous carrier (heterogeneous ionic catalysis) [19], or homogeneous catalysis under the action of an active center arising at the surface and passing out further into the gas phase (heterogeneous–homogeneous catalysis) [20].

Returning to an examination of the first of the two peculiarities of the iso synthesis referred to above, we must acknowledge the semicatalytic nature of the hydrogenation processes in iso synthesis. The semicatalytic reaction must play an important part; it provides an explanation for a number of experimental facts. First of all, it is evidently to the semicatalytic hydrogenation that the extremely high temperature required in the iso synthesis must be attributed; this temperature, 450°, is much higher than those used for the usual syntheses over nickel, cobalt (180-210°), and even iron catalysts (200-350°). The high pressure also must be attributed to the same cause; this pressure (300-600 atm) is considerably higher than that required in the synol process (iron catalyst, 18-25 atm, 190-200°), the oxo synthesis (cobalt catalyst, 150-200 atm, 190-200°), the methanol process (zinc oxide, 130 atm, 400-450°), and the synthol process (alkaline iron oxide catalyst, 150 atm, 400-500°) [5]. Semicatalytic hydrogenation in the iso synthesis must effect important changes in the initial stages of the process. Whereas on catalysts containing Group VIII metals the carbon monoxide molecule rapidly passes, through two hydrogenation stages, via the CHOH group to the CH_2 radical according to equations (1) and (2) (above), on the nonhydrogenating catalyst of the iso synthesis the second stage of the hydrogenation may not occur for all of the CHOH groups, which in this case may be formed in two ways:



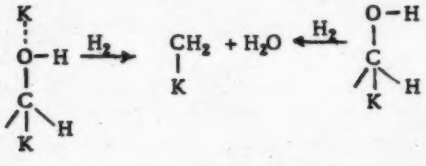
(10)

or



(11)

The difference between the CHOH groups in equations (10) and (11) is that in the first it touches two centers, and in the second, one; the position is the same for the original CO molecules. Slowness of hydrogenation may hold back the reaction at the first stage, with accumulation of appreciable amounts of CHOH groups at the catalyst surface, together with CH_2 groups. The latter are formed from CHOH groups as follows:

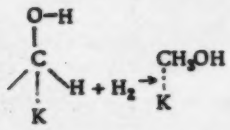


(12)

The accumulation of CHOH groups on the catalyst is of decisive significance for the further course of the reaction.

Let us consider the sort of transformation that the CHOH group can undergo. First, desorption from the surface accompanied by isomerization into formaldehyde: this process is not very probable. Then we may have semicatalytic hydrogenation with formation of a CH_2 group adsorbed on the surface; i.e., the reaction of Equation (12).

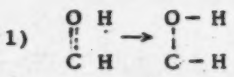
We must note further a special type of hydrogenation which the group CHOH can undergo and which does not occur when catalytic activation of hydrogen occurs, but only, evidently, by the semicatalytic method when the CHOH group is attached to only one active center (Equation 11). As a result of such a reaction a molecule of hydrogen is added with formation of methanol, which is one of the most important by-products of the iso synthesis:



(13)

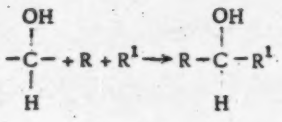
It may be supposed that the processes of Equations 11 and 13, taken together, actually express the mechanism of the synthesis of methanol from CO and H_2 on ZnO and related catalysts.

One of the most important of the other reactions that the CHOH groups may undergo is their copolymerization with CH_2 groups with formation of straight chains by reactions similar to those of Equations 3 and 4. Here we again meet a peculiar feature of the iso synthesis, as compared with the usual synthesis (in which the presence of CHOH groups in the carbon chain is exceptional, negligible amounts of oxygen compounds being formed). As early as 1946 we suggested the following scheme [3] to account for the formation of small amounts of propyl alcohol in the hydrocondensation of carbon monoxide with ethylene:



$$2)\ CH_2=CH_2 + CHOH \xrightarrow{+H_2} CH_3CH_2CH_2OH \qquad (14)$$

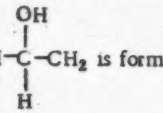
In the case of the iso synthesis, participation of CHOH groups in the formation of carbon chains is no longer the exception, but the rule. As they are bivalent, two groups R and R^1 will ultimately combine with them:



(15)

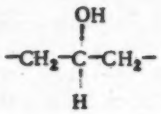
The following cases are possible:

1) If R = H and R^1 = H, the final product will be methanol. This case has already been examined above.

2) If R = H and $R^1 = CH_2$,  is formed. (16)

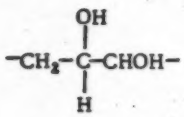
The final product after hydrogenation will be ethanol (or its higher homologs if $R^1 = CH_2{-}CH_2{-}CH_2$).

3) If $R = CH_2$ and $R^1 = CH_2$, the product will be



(17)

4) If $R = CH_2$ and R^1 = CHOH, the product will be



(18)

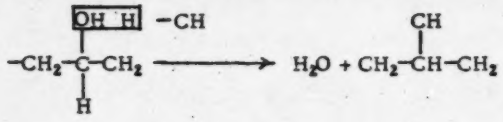
and so on.

All these groups may be more complex, since R and R^1 may be chains of methylene groups, and they may also contain CHOH groups. When we take into account the semicatalytic nature of the hydrogenation, i.e., the reaction of a complete H_2 molecule (from the gas phase), the addition of two hydrogen atoms at once to a CHOH group with formation of methanol is very probable, but addition of one hydrogen atom and one group containing a carbon atom

(Case 2) is less probable. The addition, however, of two organic groups is again very probable It follows that secondary hydroxyls will occur more frequently than primary hydroxyls in carbon chains, and this fact, as we shall see below, is of primary significance with respect to the final products of the iso synthesis. A primary hydroxyl will appear if one CHOH group unites with another CHOH. The intermediate groupings cited above may enter into further reactions.

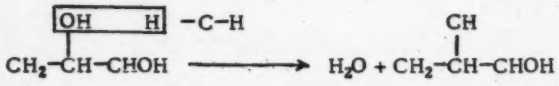
Until now polymerization by formation of new C–C bonds between CH_2 groups according to Equations 3 and 4 has been regarded as the only method by which hydrocarbon chains could be formed in the synthesis of hydrocarbons. This method undoubtedly applies also in the iso synthesis, but it is not the only method in this case.

If we consider the properties of the catalysts for this process, then it will be readily noted that they are distinguished not only by the absence of hydrogenating properties that could account for semicatalytic hydrogenation, but by powerful dehydrating effects (Al_2O_3, ThO_2, etc.), and therefore by dehydrational-condensation power. If, as we have seen, the first property is the cause of the formation of secondary hydroxyls in the carbon chains, then the second leads to the completion of the chains by condensation with elimination of water, and so to the inevitable formation of tertiary carbon atoms (cross condensation), with elimination of a hydroxyl of the chain and a hydrogen of a methylene group or, probably more rarely, a hydrogen of the chain and the hydroxyl of a CHOH group. The grouping 17, therefore, will give rise most simply and most frequently (by reaction with a methylene radical) to a species having the skeleton of isobutane, one of the main products of the iso synthesis:



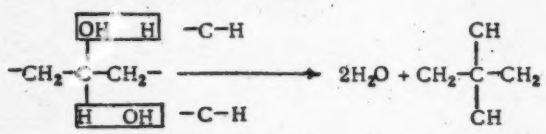
(19)

The skeleton of isobutyl alcohol, the most important oxygen compound in the iso synthesis, arises just as simply from the grouping 18 and a methlene radical:



(20)

The grouping 19 may arise partially also by the condensation of the chain $-CH_2-CH_2-CH_2$ with a CHOH group, but at the same time addition may occur also at the terminal atom of the carbon chain. There is a certain probability also of the formation of chains containing a quaternary carbon atom: from grouping 17, one CH_2 group, and one CHOH group, the neopentane grouping can be obtained:



(21)

Dehydrational condensation, as also semicatalytic hydrogenation, is slowed down by fall in temperature. Lowering the temperature to 375-400° at 300 atm therefore leads to the appearance of larger amounts of oxygen compounds, almost exclusively alcohols [21]. The yield of C_1-C_7 alcohols comprises 40-50% of the whole liquid product (apart from water) under these conditions, the yield of methanol varying from 15 to 30%, and that of isobutyl alcohol from 3 to 28% of liquid organic product.

Lowering of temperature must lead to increase in the concentration of CHOH groups and, consequently, of hydroxyl groups in the chains, and the formation of ether linkages becomes more probable:

(22)

Actually, on a catalyst consisting of 80% ThO_2 + 20% Al_2O_3 at 375° and 300 atm the yield of dimethyl ether was 66 g / cu.m, the yield of liquid hydrocarbons being 12 g/ cu.m, of gaseous hydrocarbons 10 g/ cu.m, and of methanol 7 g/ cu.m [10].

It is very interesting to note that under these conditions the average content of olefins in the hydrocarbon fraction boiling up to 150° was 76-91%, whereas for the same catalyst and the same pressure, but at 425°, it was only 34% in the fraction boiling up to 195° (although it was 62% by weight for the narrow fraction boiling at 175°-195°). It will be seen, therefore, that with rise of reaction temperature the content of unsaturated hydrocarbons is reduced. It is found also that with rise in the boiling point of fractions of a given product the content of unsaturated hydrocarbons increases and there is a simultaneous fall in the content of branched hydrocarbons. All these relation-

ships differ greatly from those observed in the usual synthesis, in which, on the contrary, rise in temperature leads to rise in the yield of unsaturated hydrocarbons, whereas, in a given product, the higher-boiling fractions are less unsaturated than the lower-boiling fractions.

All these facts are readily explained from the point of view developed above. In the usual synthesis, in which hydrogenation occurs by heterogeneous catalysis, rise in temperature favors increased dehydrogenation, resulting in an increased yield of unsaturated hydrocarbons. The higher-boiling fractions are desorbed after the lower-boiling fractions, and as a result they are more thoroughly hydrogenated. In the iso synthesis rise in temperature causes increased semicatalytic hydrogenation (a circumstance that is associated with the thermal activation of hydrogen), and this in its turn leads to an increased yield of saturated hydrocarbons. The above-mentioned relationship between the contents of olefins and of branched hydrocarbons in iso-synthesis fractions is extremely interesting: the higher the olefin content, the lower the content of iso compounds. The explanation of this may be as follows: in the long chains, dehydration at the expense of a hydroxyl and a hydrogen of a neighboring carbon atom predominates, and this leads to the formation of an olefin and also to the loss of the possibility of the formation of a side chain by cross condensation with CH_2 radicals; in short chains, on the other hand, dehydration is difficult, and this ultimately leads to dehydrational condensation with formation of a branched chain.

Increase in pressure up to 1000 atm acts in the opposite direction to increase in temperature: the result is an increased yield of oxygen compounds. Thus, over ThO_2 at 1000 atm and 400° the yield of $(CH_3)_2O$ alone was 200 g per cu.m. Under these conditions, evidently, we have almost exclusive hydrogenation of the CHOH group according to Equation 13, with subsequent ether formation according to Equation 22.

The great resemblance in the dependence of the nature of the final products on reaction temperature in the iso synthesis and the synol process [22] is worthy of note. The product of the synol process carried out at 190-200° under a pressure of 18-25 atm over Fe_2O_3 with additions of 2.5% Al_2O_3 and 0.5% K_2O contains about 50% of alcohols and 2-20% of esters. The remainder consists essentially of hydrocarbons. Over the same catalyst and at the same pressure, but at a higher temperature, 300-325°, the product consists mainly of hydrocarbons, with only 5-10% of alcohols. The iron catalyst of the synol process, unlike that of the iso synthesis, possesses hydrogenating powers, although they are considerably weaker than those of the cobalt and nickel catalysts of the usual synthesis. It is possible that, in addition to heterogeneous catalytic hydrogenation, semicatalytic hydrogenation occurs also in the synol process, which would explain the high yield of alcohols and its reduction with rise in temperature owing to increased hydrogenation on the one hand, and dehydration and dehydrational condensation on the other. There can be no doubt that the latter plays an important part in the formation of hydrocarbons of iso structure on iron catalysts, as also on the iso-synthesis catalysts, and no assumptions are necessary concerning the isomerizing properties of the two types of catalysts and the formation of branched hydrocarbons from primary hydrocarbon products of normal structure.

In just the same way, the assumption of the intermediate formation of alcohols in the iso synthesis, as made by the authors of the synthesis [21], is superfluous. These authors consider that formaldehyde is first formed from the mixture of CO and H_2, and this is further converted into methanol. Dimethyl ether is formed from methanol, and ethanol is formed from dimethyl ether. The interaction of ethanol and methanol yields isopropyl alcohol or ethyl methyl ether, which is further converted into propyl alcohol. Propyl alcohol reacts with methanol, yielding isobutyl alcohol, with ethanol, yielding 2-methyl-1-butanol, and with another molecule of propyl alcohol, yielding 2-methyl-1-pentanol. The whole of this scheme of conversions of alcohols into ethers, and these into alcohols having the same number of carbon atoms is unconvincing and does not explain the essential characteristics of the iso synthesis. We consider that the concept that we have expounded of a unified process leading, according to the conditions, to alcohols, ethers, or hydrocarbons, or to all these at the same time, is more natural and is nearer to the truth.

The conversion of dimethyl ether into hydrocarbons under the conditions of the iso synthesis [10] cannot serve as a proof of the contention of the authors of the iso synthesis, that it is an intermediate product in this synthesis [10, 2]. We may recall that it was found possible to obtain hydrocarbons from methanol, formic acid [22], and ketene [23] under the conditions of the usual synthesis over a cobalt catalyst; these results, however, did not mean that all these compounds are primary products of the synthesis.

SUMMARY

1. In the synthesis of hydrocarbons from carbon monoxide and hydrogen over nonhydrogenating oxide catalysts (Al_2O_3, ThO_2), which is called the iso synthesis, the hydrogenation processes are in the nature of semicatalytic reactions: carbon monoxide molecules are activated at the catalyst surface and are attached to the surface during the reaction, but the hydrogen molecules are thermally activated and react by moving from the gas phase, without becoming attached to the catalyst.

2. It has been suggested that semicatalytic reactions are not confined to the iso synthesis, but have a more general character.

3. In semicatalytic reactions, those atoms, in molecules attached to the catalyst, that enter the reaction must themselves be attached to the catalyst surface.

4. In the iso synthesis, CHOH groups, as well as CH_2 groups, take part in the formation of carbon chains.

5. Semicatalytic hydrogenation in the iso synthesis leads to increase in the concentration of CHOH groups and to the occurrence of hydroxyl groups at secondary carbon atoms in carbon chains.

6. Iso compounds are formed by catalytic condensation with elimination of water (dehydrational condensation).

7. The mechanism discussed readily explains the peculiar nature of the products and other experimental characteristics of the iso synthesis.

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HYDROGEN EXCHANGE BETWEEN SATURATED HYDROCARBONS AND SULFURIC ACID

D. N. Kursanov, V. N. Setkina, and O. D. Sterligov

The question of the reactivity of saturated compounds and of the relation of their reactivity to their chemical structure is a very important, but insufficiently studied topic of organic chemistry. The unsaturated hydrocarbons, constitute a particularly interesting object for investigation, for in the molecules of these substances the mutal effects of atoms are not complicated by additional effects due to hetero atoms and multiple bonds. One of the most interesting of the chemical reactions of hydrocarbons is the reaction of hydrogen-isotope exchange. Owing to the almost complete identity of the molecules of the initial and final substances, these reactions are the simplest reactions of hydrocarbons and are of particular significance for the formulation of theories of the reactivity of saturated organic compounds.

The tendency of hydrocarbons to undergo hydrogen exchange under the action of acids, particularly deuterium-enriched sulfuric acid, has not received systematic study until recently. Individual examples described in the literature lead to contradictory conclusions concerning the tendency of saturated hydrocarbons to under exchange [1]. This fact prompted us to carry out a systematic study of the tendency of hydrogen atoms in saturated organic compounds to undergo exchange under the action of acids. We have recently published a short paper [2], giving some of our results, and also a discussion of the mechanism of the hydrogen-exchange reactions of saturated hydrocarbons.

In the present paper a more detailed description is given of the results of our studies of the exchange reactivity of saturated hydrocarbons in presence of deuterium-rich sulfuric acid. These experiments were generally carried out under the following conditions: Heavy sulfuric acid (monohydrate), prepared by reaction of equimolecular amounts of sulfur trioxide and heavy water, was mixed with the hydrocarbon and shaken in a sealed tube at 20-25° in a shaker having a frequency of 150-180 per minute. At the end of the experiment the hydrocarbon was separated, freed from traces of sulfuric acid by washing with 30% aqueous caustic potash and distilled water, dried with potassium carbonate, and distilled over sodium.

It is interesting to note that in experiments with exchange-reactive hydrocarbons the sulfuric acid acquired a cherry-red or reddish-orange color, which largely disappeared on dilution with water; in some of the experiments with exchange-reactive hydrocarbons, the formation of small amounts of sulfur dioxide was observed. The distilled hydrocarbon was submitted to combustion over incandescent copper oxide in a current of dry air, and the density of the water obtained, after suitable purification, was determined by the flotation method [3].

The saturated hydrocarbons investigated for exchange reactivity had carbon skeletons of various types: hydrocarbons of normal structure (heptane and dodecane), hydrocarbons containing a tertiary carbon atom (3-methylpentane and 3-methylhexane), a hydrocarbon containing a quaternary carbon atom (2,2-dimethylhexane), and hydrocarbons containing both a tertiary and a quaternary carbon atom (2,2,3-trimethylbutane and 2,2,4-trimethylpentane).

All the hydrocarbons employed in our experiments were carefully purified by distillation through colums of 40-75 theoretical plates and passage through a layer of silica gel. The constants of the original hydrocarbons are given in Table 1.

TABLE 1

Hydrocarbon	B. p. (°C) (pressure in mm Hg)	n_D^{20}	d_4^{20}
Heptane	98.2-98.3 (760)	1.38766	0.6837
Dodecane	114.0-114.1 (27.5)	1.4221	0.7492
3-Methylpentane	63.4-63.5 (757)	1.37651	0.6644
3-Methylhexane	91.5 (745)	1.3887	0.6871
2,2-Dimethylhexane	105.8-106.0 (745)	1.3937	0.6953
2,2,3-Trimethylbutane	80.6-80.8 (760)	1.38921	0.6902
2,2,4-Trimethylpentane	99.1-99.5 (760)	1.3915	0.6931

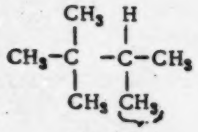
The results of our investigations are given in Table 2.

TABLE 2

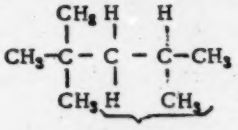
Expt. No.	Hydrocarbon	No. of moles		Duration of reaction (hrs)	Density excess of combustion water from hydrocarbon (γ)			Exchange (% of value calculated for exchange of all H)	
		of acid	of hydrocarbon		calculated*		found		
					for 1 H	for all H			
1	Heptane	0.045	0.023	1	—	3180	25	0.8	
2	Heptane	0.048	0.025	5	—	3069	34	1.1	
3	Heptane	0.050	0.018	10	—	4140	24	0.6	
4	Heptane	0.057	0.021	50	—	4112	70	1.7	
5	Dodecane	0.037	0.008	4	—	2346	28	1.2	
6	3-Methylpentane	0.052	0.017	5	806	4348	4206	96.8	
7	3-Methylpentane	0.059	0.017	10	957	5106	4945	96.9	
8	3-Methylhexane	0.052	0.022	11	799	3527	3392	96.2	
9	2,2-Dimethylhexane	0.051	0.029	4	—	3198	74	2.3	
10	2,2,3-Trimethylbutane	0.058	0.024	5	17042 (for 7 H)	22272	16410	96.3	of 7 H
11	2,2,3-Trimethylbutane	0.052	0.022	10	16616 (for 7 H)	21502	15170	91.3	of 7 H
12	2,2,3-Trimethylbutane	0.044	0.020	25	15776 (for 7 H)	20116	20180	100	
13	2,2,4-Trimethylpentane	0.062	0.018	1	3454 (for 9 H)	4461	478	10.7	
14	2,2,4-Trimethylpentane	0.069	0.018	2	3420 (for 9 H)	4397	1293	29.4	
15	2,2,4-Trimethylpentane	0.070	0.021	3	3215 (for 9 H)	4085	1685	41.2	
16	2,2,4-Trimethylpentane	0.059	0.018	14	3185 (for 9 H)	4022	2463	60.0	
17	2,2,4-Trimethylpentane	0.035	0.017	12	14724 (for 9 H)	17443	14660	99.6	of 9 H
18	2,2,4-Trimethylpentane	0.047	0.020	25	16221 (for 9 H)	19604	18248	93.1	

These results indicate the great difference in behavior of hydrocarbons of different structures. It will be seen from Table 2 that hydrocarbons whose molecules contain only primary, secondary, and quaternary carbon atoms practically do not enter into the hydrogen-exchange reaction (Expts. 1, 2, 3, 4, 5, and 9). On the other hand, hydrocarbons whose molecules contain a tertiary carbon atom (even if only one) show exchange reactivity, and it should be noted that all the hydrogen atoms of the molecule evidently take part in the exchange (Expts. 6, 7, and 8), and that exchange equilibrium is established extremely readily (in several hours at room temperature).

Hydrocarbons containing both tertiary and quaternary carbon atoms also take part in the exchange reaction and exchange all their hydrogen atoms for deuterium after a sufficiently long period. Under the conditions, however, under which 3-methylpentane and 3-methylhexane exchange all their hydrogen for deuterium (Expts. 6, 7, and 8), 2,2,3-trimethylbutane exchanges only 7 of its 16 hydrogen atoms for deuterium (Expts. 10 and 11), and 2,2,4-trimethylpentane exchanges 9 out of 18 hydrogen atoms; these results correspond to the exchange of all hydrogen atoms that occur in the molecule up to the quaternary carbon atom (Formulas 1 and 2):



(1) 7 H



(2) 9 H

When the experiments are prolonged further all the hydrogen atoms of 2,2,3-trimethylbutane and 2,2,4-trimethylpentane are exchanged for deuterium (Expts. 12 and 18), and this is probably associated with the isomerization of the hydrocarbons under these conditions. The isomerization of hydrocarbons of this type in presence of concentrated sulfuric acid was studied recently by Komarewsky and Ruther [4]. An indirect confirmation of the occurrence of isomerization is afforded by the changes in the constants of 2,2,4-trimethylpentane when subjected to prolonged contact with sulfuric acid (see description of experiments).

When the present investigation had been completed, and simultaneously with the publication of our first communication [2], there appeared a paper by Stevenson, Wagner, Beeck, and Otvos in the Journal of American Chemical Society [5] which was also devoted to a study of the hydrogen exchange of saturated hydrocarbons under the action of sulfuric acid. The results obtained by these authors agree, in the main, with ours, and they confirm the high tendency

* In the calculation the distribution coefficient was taken to be unity.

for hydrogen atoms to undergo exchange in the molecules of saturated hydrocarbons containing one or more tertiary carbon atoms.

It must be pointed out that Stevenson, Wagner, Beeck, and Otvos differ from us in their conclusions regarding the number of hydrogen atoms taking part in the exchange reactions of hydrocarbons. They assert that all the hydrogen atoms take part in the exchange, with the exception of hydrogen atoms attached to tertiary carbons.

It should be noted that in the experiments of these authors the time of contact of the hydrocarbons with sulfuric acid was considerably shorter than in our experiments, and as a result the great majority of the molecules would succeed in assuming the ionic state on not more than one occasion. These conditions are essentially different from ours. The examples that we investigated do not permit us to make a completely unequivocal choice between the two possibilities indicated, because of the closeness of the density excess values calculated for exchange equilibrium with participation of all of the hydrogen atoms or of one less than this number. The question, therefore, of whether all of the hydrogen atoms of a hydrocarbon participate in exchange equilibrium, under the conditions of prolonged contact with sulfuric acid, requires further investigation.

EXPERIMENTAL*

1. Heptane and Heavy Sulfuric Acid

Heavy sulfuric acid was prepared from sulfur trioxide and water enriched in deuterium oxide. In this way samples of anhydrous sulfuric acid (containing in certain cases up to 2% of sulfur trioxide) having various equivalent density excesses were obtained. Heptane, b.p. 98.2-98.3°/ 760 mm, d_4^{20} 0.6837 and n_D^{20} 1.38766, was prepared from heptane of standard quality by washing with concentrated sulfuric acid, drying with calcium chloride, distillation through a 40-plate column, and final purification through a silica gel column.

A. A mixture of 2.30 g (0.023 mole) of heptane and 4.49 g (0.045 mole) of heavy sulfuric acid (equivalent density excess 17,000 γ) was shaken in a sealed tube in a shaker of frequency 150-180 per minute for one hour. The contents of the tube were separated in a separating funnel, and the hydrocarbon layer was washed with 30% aqueous caustic potash and with water. It was then dried with potassium carbonate and distilled over sodium. The hydrocarbon was submitted to combustion over incandescent copper oxide, and the water produced was purified by our usual method [3]. The density excess of the water was determined by a densiometric method, the value obtained for the combustion water of heptane being 25 γ; the value calculated for the exchange of all 16 hydrogen atoms was 3180 γ.

B. A mixture of 2.51 g (0.025 mole) of heptane and 4.69 g (0.048 mole) of heavy sulfuric acid was agitated in a sealed tube for five hours. The contents of the tube were then treated as in Expt. A. The excess density of the combustion water of the heptane was found to be 34 γ, and the value calculated for full exchange of all of the hydrogen atoms was 3069 γ.

C. A mixture of 1.80 g (0.018 mole) of heptane and 4.95 g (0.050 mole) of heavy sulfuric acid was agitated for ten hours. The excess density of the combustion water of the heptane after the experiment was 24 γ, and the value calculated for full exchange of all of the hydrogen atoms was 4140 γ.

D. A mixture of 2.05 g (0.021 mole) of heptane and 5.59 g (0.057 mole) of heavy sulfuric acid was agitated for 50 hours. The value found for the excess density of the combustion water of the heptane was 70 γ, and the value calculated for the exchange of all of the hydrogen atoms was 4112 γ. The results of the experiments show that heptane practically does not undergo hydrogen exchange with sulfuric acid.

2. Dodecane and Heavy Sulfuric Acid

Dodecane was obtained from hexyl alcohol by converting it into hexyl bromide, and then by the Wurtz reaction into dodecane. The hydrocarbon was vacuum-distilled through a column of 75-80 theoretical plates, and it had the following constants: b.p. 114.0-114.1°/ 27.5 mm, d_4^{20} 0.7492; n_D^{20} 1.4221.

A mixture of 1.27 g (0.008 mole) of dodecane and 3.63 g (0.037 mole) of fuming heavy sulfuric acid (equiv. density excess 17,000 γ) was agitated in a sealed tube for four hours. After the experiment, the constants of the hydrocarbon were: b.p. 115-115.5°/ 32 mm, $n_D^{20.3}$ 1.4219; $d_4^{20.2}$ 0.7486. The density excess of the combustion water of dodecane was 28 γ, instead of the value required by calculation for the exchange of all of the hydrogen atoms, 2346 γ. These results show that under these conditions dodecane is not exchange reactive.

*Laboratory worker A. N. Martynova assisted in the experimental work.

3. 3-Methylpentane and Heavy Sulfuric Acid

3-Methylpentane was prepared by hydrogenation in presence of a platinum catalyst [6] of the mixture of olefins obtained by the dehydration of 3-methyl-3-pentanol. It was distilled through a 40-plate column, and it had the following constants: b.p. 63.4-63.5°/ 757 mm, n_D^{20} 1.37651, and d_4^{20} 0.6644.

A. A mixture of 1.60 g (0.017 mole) of 3-methylpentane and 5.08 g (0.052 mole) of heavy sulfuric acid (equiv. density excess 15,350 γ) was agitated for five hours. After the experiment the constants of the hydrocarbon were: b.p. 60.5-61.5°/ 756 mm; n_D^{20} 1.3748; d_4^{20} 0.6638. The changes in the constants indicate that partial isomerization of the 3-methylpentane had occurred. The density excess found for the combustion water from 3-methylpentane was 4206 γ, and the calculated value for exchange of all hydrogen atoms was 4348 γ.

B. A mixture of 1.45 g (0.017 mole) of 3-methylpentane and 5.79 g (0.059 mole) of heavy sulfuric acid (15,350 γ) was agitated in a sealed tube for ten hours. After the experiment the constants of the hydrocarbon were: n_D^{20} 1.3742 and d_4^{20} 0.6640. The combustion water from the hydrocarbon had an excess density of 4945 γ, the value calculated for exchange of all hydrogen atoms being 5106 γ. The two experiments show that 3-methylpentane undergoes hydrogen exchange with sulfuric acid.

4. 3-Methylhexane and Heavy Sulfuric Acid

3-Methylhexane was prepared as follows. 3-Methyl-3-hexanol was prepared from 2-butanone and propyl bromide by the Grignard reaction, and was then dehydrated to give 3-methylhexene. This substance was hydrogenated at atmospheric pressure and room temperature in presence of platinized charcoal activated with chloroplatinic acid [6]. The 3-methylhexane was distilled through a 40-plate column; it had the following constants: b.p. 91.5°/ 745 mm; n_D^{20} 1.3887; d_4^{20} 0.6871.

A. A mixture of 2.20 g (0.022 mole) of 3-methylhexane and 5.10 g (0.052 mole) of fuming heavy sulfuric acid (15,500 γ) was agitated in a sealed tube for 11 hours. After the experiment the hydrocarbon was purified in the usual way; it had the following constants: b.p. 89.5-90°/ 749 mm; n_D^{20} 1.3881; d_4^{20} 0.6883. The excess density of the combustion water from the 3-methylhexane was 3392 γ, instead of 3527 γ required for exchange of all hydrogen atoms.

B. A mixture of 4.14 g (0.041 mole) of 3-methylhexane and 4.36 g (0.044 mole) of heavy sulfuric acid (110,520 γ) was heated in a sealed tube at 119-120° for 23 hours. The density excess of the combustion water from the hydrocarbon was 3600 γ instead of 12,850 γ, as required by calculation for exchange of all hydrogen atoms. These results indicate that 3-methylhexane is exchange reactive.

5. 2,2-Dimethylhexane and Heavy Sulfuric Acid

2,2-Dimethylhexane was prepared as follows. The Grignard reaction with tert-butylmagnesium chloride and butyraldehyde yielded 2,2-dimethyl-3-hexanol, which was acetylated with acetyl chloride in presence of barium carbonate. The acetate obtained was subjected to pyrolysis at 450°. The 2,2-dimethyl-3-hexene isolated from the pyrolysis products was hydrogenated in presence of a platinum catalyst [6]. The 2,2-dimethylhexane was distilled through a 40-plate column; it had the constants: b.p. 105.8-106.0°/ 745 mm; d_4^{20} 0.6953; n_D^{20} 1.3937.

A. A mixture of 3.25 g (0.029 mole) of 2,2-dimethylhexane and 5.85 g (0.051 mole) of heavy sulfuric acid (17,000 γ) was agitated for four hours. After the experiment the constants of the hydrocarbon were: b.p. 105.5°/ 745.5 mm; n_D^{20} 1.3937; d_4^{20} 0.6953. The value found for the density excess of its combustion water was 74 γ, and the value calculated for exchange of all hydrogen atoms was 3198 γ.

B. A mixture of 3.45 g (0.030 mole) of 2,2-dimethylhexane and 6.74 g (0.067 mole) of heavy sulfuric acid (92,000 γ) was heated in a sealed tube for five hours at 130° and 17.5 hours at 145-150°. After the experiment the hydrocarbon was purified in the usual way. The density of the combustion water from the 2,2-dimethylhexane corresponded to that of standard water. It follows from these experiments that 2,2-dimethylhexane, which has no tertiary carbon atoms, also has no exchange reactivity.

6. 2,2,3-Trimethylbutane and Heavy Sulfuric Acid

2,2,3-Trimethylbutane was prepared as follows. Pinacolone and methyl bromide were converted by the Grignard reaction into 1,1,2,2-tetramethylpropanol, which was dehydrated to give 2,2,3-trimethyl-3-butene. This substance was then hydrogenated under pressure at 160-170° in presence of a nickel catalyst, and the 2,2,3-trimethylbutane obtained was distilled and purified by passage through a silica gel column. The constants of the 2,2,3-trimethylbutane were: b.p. 80.6-80.8°/ 760 mm; d_4^{20} 0.6902; n_D^{20} 1.38921.

A. A mixture of 2.35 g (0.024 mole) of 2,2,3-trimethylbutane and 5.82 g (0.058 mole) of heavy sulfuric acid (94,000 γ) was agitated for five hours. After the experiment the hydrocarbon was purified in the usual way and had the following constants: b.p. 79.5-80.5°/ 760 mm; d_4^{20} 0.7074; n_D^{20} 1.3882. The value found for the excess density of the combustion water from 2,2,3-trimethylbutane was 16,410 γ, and the value calculated for exchange of all hydrogen atoms was 22,272 γ, and for the exchange of 7 hydrogen atoms (the number occurring up to the barrier formed by the quaternary carbon atom) —17,042 γ.

B. A mixture of 2.20 g (0.022 mole) of 2,2,3-trimethylbutane and 5.22 g (0.052 mole) of heavy sulfuric acid (94,000 γ) was agitated for ten hours. After the experiment the hydrocarbon had the following constants: d_4^{20} 0.7072; n_D^{20} 1.3883. The density excess of the combustion water from the hydrocarbon was 15,170 γ, and the value calculated for exchange of 7 hydrogen atoms was 16,616 γ, and for exchange of all hydrogen atoms —21,502 γ.

C. A mixture of 2.02 g (0.020 mole) of 2,2,3-trimethylbutane and 4.40 g (0.044 mole) of heavy sulfuric acid (94,000 γ) was agitated for 25 hours. After the experiment the hydrocarbon had the following constants: b.p. 79.5-80°/ 760 mm; d_4^{20} 0.7114; n_D^{20} 1.3880. The density excess of the combustion water from the hydrocarbon was 20,180 γ, the calculated values being 15,776 γ for exchange of 7 hydrogen atoms and 20,116 γ for exchange of all hydrogen atoms. The experiments show that the first seven hydrogen atoms undergo exchange more readily than the remainder.

7. 2,2,4-Trimethylpentane and Heavy Sulfuric Acid

2,2,4-Trimethylpentane was prepared from "isooctane" of standard quality by distillation through a 40-plate column, followed by purification in a silica gel column. It had the constants: b.p. 99.6-99.7°/ 760 mm; d_4^{20} 0.6908; n_D^{20} 1.3914.

A. A mixture of 1.72 g (0.015 mole) of 2,2,4-trimethylpentane and 10.27 g (0.104 mole) of fuming heavy sulfuric acid (17,000 γ) was agitated for 2 hours 30 minutes. The hydrocarbon dissolved to an appreciable extent in the sulfuric acid, and the sulfuric acid layer acquired an intense reddish-orange coloration. The 2,2,4-trimethylpentane, after the usual purification treatment, was subjected to combustion, and the density excess of the combustion water was 7590 γ, the value calculated for exchange of all hydrogen atoms being 7390 γ.

B. A mixture of 2.04 g (0.018 mole) of 2,2,4-trimethylpentane (b.p. 99.1-99.5°/ 760 mm; d_4^{20} 0.6931; n_D^{20} 1.3915) and 6.10 g (0.062 mole) of heavy sulfuric acid (15,300 γ) was agitated for one hour. After the experiment the hydrocarbon had b.p. 98.5-99°; d_4^{20} 0.6923, n_D^{20} 1.3915. The density excess of the combustion water from the 2,2,4-trimethylpentane was 478 γ; the value calculated for exchange of 9 hydrogen atoms was 3454 γ, and for the exchange of all 18 atoms —4461 γ.

C. A mixture of 2.09 g (0.018 mole) of 2,2,4-trimethylpentane and 6.67 g (0.069 mole) of heavy sulfuric acid was agitated for two hours. After the experiment the hydrocarbon had b.p. 97.5-100°/ 760 mm; d_4^{20} 0.6936; n_D^{20} 1.3913. The density excess of the combustion water from the 2,2,4-trimethylpentane was 1293 γ; the value calculated for exchange of 9 hydrogen atoms was 3420 γ, and for the exchange of all hydrogen atoms —4397 γ.

D. A mixture of 2.37 g (0.021 mole) of 2,2,4-trimethylpentane and 6.86 g (0.070 mole) of heavy sulfuric acid was agitated for three hours. After the experiment the hydrocarbon had b.p. 97-104°(760 mm); d_4^{20} 0.6914; n_D^{20} 1.3912. The density excess of the combusion water from the 2,2,4-trimethylpentane was 1685 γ; the value calculated for exchange of 9 hydrogen atoms was 3215 γ, and for all hydrogen atoms —4085 γ.

E. A mixture of 2.03 g (0.018 mole) of 2,2,4-trimethylpentane and 5.79 g (0.059 mole) of heavy sulfuric acid was agitated for 14 hours. After the experiment the constants of the hydrocarbon were: 96.5-104°; d_4^{20} 0.6948; n_D^{20} 1.3937. The value found for the density excess of the combustion water from the hydrocarbon was 2463 γ; the value calculated for exchange of 9 hydrogen atoms was 3185 γ, and for exchange of all hydrogen atoms —4022 γ.

F. A mixture of 1.94 g (0.017 mole) of 2,2,4-trimethylpentane and 3.49 g (0.035 mole) of heavy sulfuric acid (94,000 γ) was agitated for 12 hours. After the experiment the constants of the hydrocarbon were: b.p. 97-108°; d_4^{20} 0.7148; n_D^{20} 1.3954. The value found for the density excess of the combustion water was 14,660 γ; the value calculated for exchange of 9 hydrogen atoms was 14,724 γ, and for exchange of all 18 hydrogen atoms —17,443 γ.

G. A mixture of 2.24 g (0.020 mole) of 2,2,4-trimethylpentane and 4.66 g (0.047 mole) of heavy sulfuric acid (94,000 γ) was agitated for 25 hours. After the experiment the constants of the hydrocarbon were: b.p. 97-115°; d_4^{20} 0.7225; n_D^{20} 1.3965. The density excess of the combustion water was 18,248 γ; the value calculated for exchange of 9 hydrogen atoms was 16,221 γ, and for exchange of all hydrogen atoms —19,604 γ.

On the basis of the experiments on exchange with 2,2,4-trimethylpentane, it follows that simultaneously with the exchange of hydrogen for deuterium atoms isomerization of the 2,2,4-trimethylpentane occurs. These results,

as also the results of the preceding series of experiments, confirm that hydrogen atoms occurring on one side of a quaternary carbon (namely, the side containing the tertiary carbon) enter into the hydrogen exchange reaction more readily than the remaining hydrogen atoms.

We express our deep gratitude to A. L. Liberman for providing us with dodecane and 3-methylhexane required in our investigations, and to A. P. Meshcheryakov for providing 2,2,3-trimethylbutane.

SUMMARY

1. An investigation has been made into the exchange reactivity of the hydrogen atoms of saturated acyclic hydrocarbons under the action of sulfuric acid-d_2, the hydrocarbons studied being heptane, dodecane, 3-methylpentane, 3-methylhexane, 2,2-dimethylhexane, 2,2,3-trimethylbutane, and 2,2,4-trimethylpentane.

2. It has been established that only hydrocarbons containing a tertiary carbon atom enter into the exchange reaction with heavy sulfuric acid. For these hydrocarbons, exchange equilibrium is attained in a few hours at 20-25°.

3. It has been established that hydrogen atoms in saturated acyclic hydrocarbons containing tertiary carbon atoms have high mobility and are able to undergo exchange with deuterium in presence of heavy sulfuric acid.

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TRANSFORMATIONS OF VINYL ETHERS

SYNTHESIS OF HALO ACETALS FROM VINYL ETHERS

M. F. Shostakovsky and N. A. Gershtein

This paper describes the continuation of an investigation on the addition of chlorohydrins to alkyl vinyl ethers [1]. The reaction proceeds as follows:

$$CH_2{=}CH{-}OR + HOCH_2CH_2Cl \rightarrow CH_3CH(OR)OCH_2CH_2Cl.$$

The object of the investigation was a study of the effect of the nature of the halogen-substituted radicals in alkyl haloalkyl acetals on the tendency of these mixed acetals to undergo the disproportionation reaction that we have previously observed for mixed dialkyl acetals [2, 3]. The presence of halogen in these compounds may also be of interest for its own sake, since it makes it possible to pass to other series of compounds prepared by replacement of halogen by other functional groups [4].

The synthesis of alkyl 2-chloroethyl acetals has been developed and described by us previously, two examples being given [1]. We have now applied this method, which is extremely simple and may be carried out without the use of catalysts, to the synthesis of five new homologs Our starting materials were alkyl vinyl ethers and 2-chloroethanol. The alkyl vinyl ethers were prepared by Favorsky and Shostakovsky's method [5] and were purified by the method developed in our laboratory [6]. 2-Chloroethanol was purified by repeated distillation. Physical constants of the starting materials are given in Table 1.

TABLE 1

Physical Constants of Starting Materials

Formula of substance	B. p. (°C) (press in mm Hg)	d_4^{20}	n_D^{20}
$CH_2 = CH-O-CH_3$	5 (744)	0.7725 (0°)	1.3730 (0°)
$CH_2 = CH-OC_3H_7$	64-65 (760)	0.7678	1.3922
$CH_2 = CH-OC_3H_7$-i	55-56 (760)	0.7518	1.3858
$CH_2 = CH-OC_4H_9$-i	82-83 (760)	0.7680	1.3960
$CH_2 = CH-OC_5H_{11}$-i	110-112 (760)	0.7822	1.4098
$HOCH_2CH_2Cl$	127.6-128 (760)	—	1.4407

EXPERIMENTAL*

The conditions of synthesis have been described in detail in the preceding communication [1]. In the case of methyl vinyl ether, some changes were necessary on account of its low boiling point (5°), and these are described below.

The synthesis of acetaldehyde 2-chloroethyl methyl acetal was carried out in a three-necked flask fitted with reflux condenser, mercury-sealed stirrer, and thermometer. 2-Chloroethanol (80 g, i.e., 1 mole) was introduced into the flask, which was cooled in an ice-salt bath to −8-10°, and methyl vinyl ether (58 g, i.e., 1 mole), previously cooled to the same temperature (the ampoule containing it was immersed in the same bath), was added in one lot through a side neck. The temperature of the reaction mixture rose rapdily to + 41°, and then soon began to fall. Stirring was continued for two hours, and the reaction mixture was then set aside overnight at room temperature. Vacuum fractionation of the reaction products yielded 80.5 g (61%) of acetaldehyde 2-chloroethyl methyl acetal, b.p. 52.0-52.9°/ 16 mm.

Details of the acetal syntheses are given in Table 2, and their physical constants are given in Table 3.

*A. K. Gorban assisted in the experimental work.

TABLE 2

Details of Acetal Syntheses

Expt. No.	Formula of vinyl ether	Amount (moles)	Formula of alcohol	Amount (moles)	Formula of acetal		Yield (% on 2-chloroethanol)		
					Desired	Symmetrical	desired	symmetrical	total
1	$CH_2=CH-O-CH_3$	1	$HOCH_2CH_2Cl$	1	$CH_3CH(OCH_3)OCH_2CH_2Cl$	$CH_3CH(OCH_3)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	61	9.6	70.6
2	$CH_2=CH-OC_3H_7$-n	1.39	$HOCH_2CH_2Cl$	1.39	$CH_3CH(OC_3H_7$-n$)OCH_2CH_2Cl$	$CH_3CH(OC_3H_7$-n$)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	66.8	7.85	74.7
3	$CH_2=CH-OC_3H_7$-i	1.5	$HOCH_2CH_2Cl$	1.5	$CH_3CH(OC_3H_7$-i$)OCH_2CH_2Cl$	$CH_3CH(OC_3H_7$-i$)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	64.8	10.02 15.70	90.52
4	$CH_2=CH-OC_4H_9$-i	1	$HOCH_2CH_2Cl$	1	$CH_3CH(OC_4H_9$-i$)OCH_2CH_2Cl$	$CH_3CH(OC_4H_9$-i$)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	77.6	8.6	86.2
5	$CH_2=CH-OC_5H_{11}$	0.23	$HOCH_2CH_2Cl$	0.23	$CH_3CH(OC_5H_{11}$-i$)OCH_2CH_2Cl$	$CH_3CH(OC_5H_{11}$-i$)_2$ $CH_3CH(OCH_2CH_2Cl)_2$	93.2	—	93.2

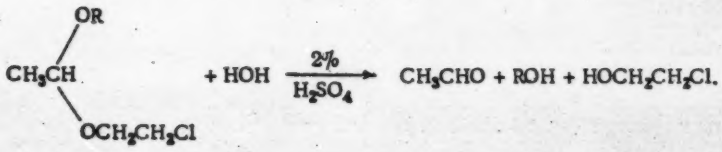
Note: In the synthesis of small amounts of material (Expt. 5) practically no disproportionation occurred. This is explained by the shorter period of heating during the distillation.

TABLE 3

Characteristics of Compounds Obtained

Formula of substance	B.p. (°C) (press. in mm Hg)	d_4^{20}	n_D^{20}	MR_D		Elementary analysis					
				Found	Calc.	C in %		H in %		Cl in %	
						Found	Calc.	Found	Calc.	Found	Calc.
$CH_3CH(OCH_3)OCH_2CH_2Cl$	52-52.9 (16)	1.0541	1.4211	33.35	33.44	43.21 42.95	43.33	8.11 8.04	8.00	25.76 25.5	25.58
$CH_3CH(OC_3H_7$-n$)OCH_2CH_2Cl$	55-57 (9)	0.9969	1.4232	42.79	42.68	50.93 51.07	50.45	9.53 9.18	9.07	21.26 21.20	21.28
$CH_3CH(OC_3H_7$-i$)OCH_2CH_2Cl$	42.5-44 (2)	0.9948	1.4218	42.55	42.68	50.40 50.36	50.45	8.84 8.96	9.07	20.96 21.10	21.28
$CH_3CH(OC_4H_9$-i$)OCH_2CH_2Cl$	68-69 (7)	0.9796	1.4245	47.11	47.30	53.42 53.18	53.18	9.08 9.17	9.48	19.09 19.01	19.63
$CH_3CH(OC_5H_{11}$-i$)OCH_2CH_2Cl$	60-63 (1.5)	0.9672	1.4312	52.12	51.92	55.61 55.67	55.52	9.92 9.96	9.84	18.29 18.42	18.21
$CH_3CH(OCH_2CH_2Cl)_2$	105.5-106 (12.5)	1.1793	1.4529	42.87	42.93	38.20 38.33	38.52	6.72 6.74	6.47	—	—
$CH_3CH(OC_3H_7$-i$)_2$	125.5-127.5 (360)	0.8158	1.3900	42.50	42.43	65.17 65.35	65.71	12.67 12.49	12.41	—	—

The structure of the acetals obtained was proved by hydrolysis with 2% sulfuric acid [7]. The reaction proceeds as follows:



The acetaldehyde formed was taken up with 0.2 N sodium bisulfite, the excess of which was titrated with 0.1 N iodine. Calculation was by the formula:

$$\% \text{ acetal} = \frac{K(a-b)M}{200w}$$

where K is the correction factor, a is the amount of iodine (ml) required in a control experiment, b is the amount of iodine (ml) used in the titration of the excess of bisulfite, M is the molecular weight of the acetal, and w is the amount of acetal taken. The hydrolysis results are given in Table 4.

TABLE 4

Hydrolysis of Acetals and Their Quantitative Determination in Terms of CH_3CHO

Formula of substance	Amount taken (g)	Amount of 0.1 N I_2 equiv. to bisulfite taken up	CH_3CHO found (% of theoretical)	Correction factor of 0.1 N I_2
$CH_3CH(OCH_3)OCH_2CH_2Cl$	0.1931	27.6	98	
	0.1529	22	98.7	0.9899
	0.1481	21.3	98.6	
$CH_3CH(OC_3H_7\text{-n})OCH_2CH_2Cl$	0.1436	13.6	98	0.98692
	0.2358	17.3	99.1	
$CH_3CH(OC_3H_7\text{-i})OCH_2CH_2Cl$	0.1976	23.85	99.3	0.98692
	0.2040	24.45	99.8	
$CH_3CH(OC_4H_9\text{-i})OCH_2CH_2Cl$	0.2862	31.9	99.4	0.98692
	0.1328	14.8		
$CH_3CH(OC_5H_{11}\text{-i})OCH_2CH_2Cl$	0.1316	13.6	99.3	0.98692
	0.1637	16.8	98.6	

SUMMARY

1. A study has been made of the addition of 2-chloroethanol to alkyl vinyl ethers.

2. It has been shown that the reaction is brought about in a very simple manner—by mixing equimolecular amounts of the components—and is accompanied by an exothermic effect.

3. Five new alkyl 2-chloroethyl acetals have been prepared: the 2-chloroethyl methyl, 2-chloroethyl propyl, 2-chloroethyl isopropyl, 2-chloroethyl isobutyl, and 2-chloroethyl isopentyl acetals of acetaldehyde.

4. These acetals, like other mixed acetals, are able to undergo disproportionation with formation of two symmetrical, dialkyl and bis(2-chloroethyl), acetals.

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CHEMICAL REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 1. COPOLYMERIZATION OF METHACRYLIC ACID AND ALKYL VINYL ETHERS

M. F. Shostakovsky and A. M. Khomutov

Among the numerous methods of preparing macromolecular compounds, the copolymerization reaction occupies a special place. It is an extremely valuable synthetic method, permitting the preparation of macromolecular compounds having the most varied properties. In this reaction, various unsaturated compounds may be used as starting materials. By variation in the ratio of initial components and in the conditions of copolymerization, macromolecular compounds differing in composition, structure, and properties, can be obtained.

The simplest case of copolymerization is found when two unsaturated compounds react to form macromolecules having different alternating units:

$$n(CH_2 = CHOR) + m(CH_2 = CHOR_1) \rightarrow \cdots -CH_2-\underset{\underset{OR}{|}}{CH}-CH_2-\underset{\underset{OR_1}{|}}{CH}-\cdots \qquad (I)$$

Copolymers of such regular structure, however, are exceptional.

Convincing proof of the above statements is to be found in the example of copolymerization of compounds of the same homologous series [1]. It was here established that the formation of the copolymer and its composition was determined by the activity of the initial monomers.

If due consideration is given to the method of copolymerization in the widest sense of the word, then we consider that the synthetic methods for the preparation of macromolecular compounds can be widened still further, if for this purpose not only multiple bonds are utilized, but also the functional groups of the starting substances, e.g. OH, COOH, NH_2, SH, etc. We have accordingly undertaken an investigation into the copolymerization of compounds of the following structures:

$$CH_2 = C(CH_3)COOH;\ CH_2 = CHOAlk;\ CH_2 = CHOAr;$$

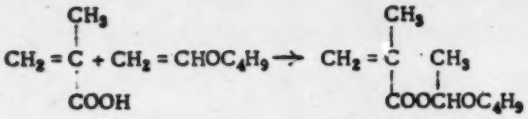
$$CH_2 = CHOCH_2CH_2NH_2\ [2];\ CH_2 = CHOCH_2CH_2OH\ [3];\ \text{etc.}$$

It is known from the literature [4, 5] that in the interaction of unsaturated compounds containing functional groups, or devoid of such groups, a number of competing reactions occur. Among these reactions, the most notable are polymerization and copolymerization processes in which multiple bonds take part [6]:

$$n\left(CH_2 = \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right) + m(CH_2 = CHC_6H_5) \rightarrow$$

$$\rightarrow \cdots - \left[-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\right]_{n_1} - \left[-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-\right]_{m_1} -\cdots \qquad (II)$$

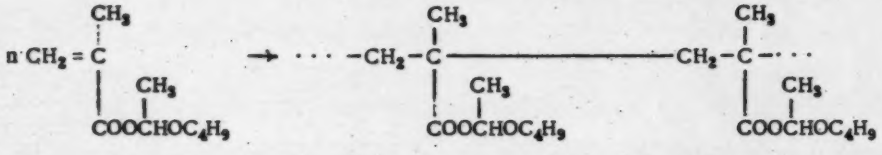
Among other forms of interaction between unsaturated compounds, we must refer to the reactions in which both multiple bonds and functional groups participate. In such cases the reactions may proceed in such a way that at first addition products are formed [7], e. g. 1-alkoxyethyl methacrylate:



(III)

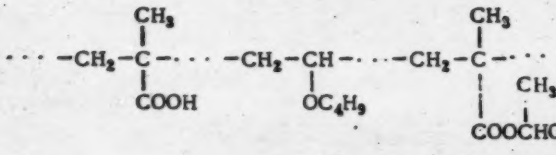
and then the following processes occur:

a) polymerization:



(IV)

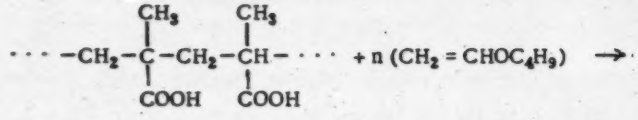
b) copolymerization of the original and newly formed compounds:

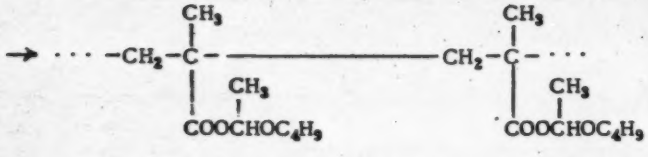


(V)

It will be clear from the above that, with these reactions at our command, the synthetic methods available for effecting transformations of unsaturated compounds are greatly extended.

The synthesis of macromolecular compounds is therefore widened in scope by reactions in which not only multiple bonds, but also functional groups take part. This method enables us to prepare macromolecular products having a variety of structures. It can be applied not only to the original monomers, but also to macromolecular compounds, as illustrated by the example of polymethacrylic acid and an alkyl vinyl ether, when the reaction may proceed as follows:

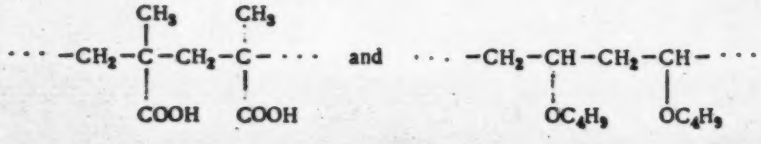




(VI)

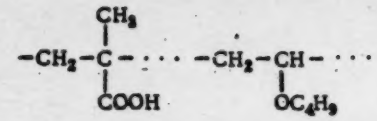
These examples enable us to make a wider and deeper examination of the processes occurring in the reactions of compounds having both multiple bonds and functional groups. Our discussion may be illustrated by the following schemes:

1) Polymerization of the original monomers:



(VII and VIII)

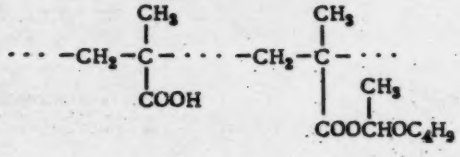
2) Copolymerization of the original monomers:



(IX)

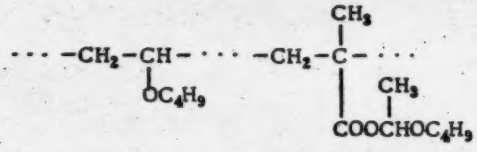
3) Formation of acylals, and their polymerization (III and IV).

4) Copolymerization of methacrylic acid with an acylal:



(X)

5) Copolymerization of alkyl vinyl ether with an acylal:



(XI)

6) Copolymerization of the original monomers and an acylal (V).

7) Addition of alkyl vinyl ether to a carboxyl group of the polymer or copolymer (VI).

The reaction of methacrylic acid with vinyl ethers is a convenient one for the preparation of macromolecular compounds having different contents of carboxyl groups.

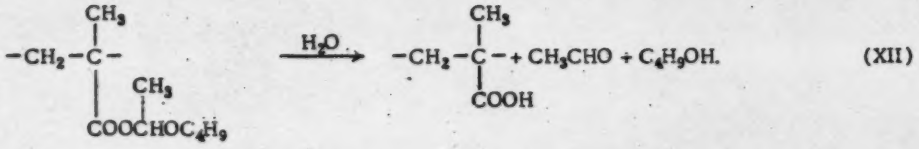
The composition and structure of copolymers of methacrylic acid with alkyl vinyl ethers (and also with acylals) were determined by elementary microanalysis, titration of free carboxyl groups, hydrolysis, and solubility determinations. The compositions of the copolymers are given in Table 1.

TABLE 1
Analytical Results for Copolymers

Monomers	Amounts (moles)	Content of		Acid and ether units in the copolymer		Fraction of possible carboxyls found (%)
		C (%)	H (%)	% by wt.	mole-%	
$CH_2=C(CH_3)COOH$	3	57.25	7.51	86.7	83.7	87.48
$CH_2=CHOC_2H_5$	1			13.3	16.3	
$CH_2=C(CH_3)COOH$	1	57.83	7.57	81.2	79.94	80.89
$CH_2=CHOC_2H_5$	1			18.8	20.06	
$CH_2=C(CH_3)COOH$	1	60.50	8.34	55.8	51.37	69.78
$CH_2=CHOC_2H_5$	3			44.2	48.63	
$CH_2=C(CH_3)COOH$	3	58.64	7.37	82.5	84.57	83.86
$CH_2=CHOC_4H_9$	1			17.5	15.43	
$CH_2=C(CH_3)COOH$	1	59.60	7.33	76.6	79.20	76.04
$CH_2=CHOC_4H_9$	1			23.4	20.80	
$CH_2=C(CH_3)COOH$	1	59.65	8.31	76.3	78.92	70.02
$CH_2=CHOC_4H_9$	3			23.7	21.08	

It will be seen from Table 1 that with increase in the amount of alkyl vinyl ether the carbon content of the copolymer increases. The dependence of the composition of the copolymer on the ratio of the original components is to be seen particularly clearly when 1 mole of methacrylic acid and 3 moles of ethyl vinyl ether are used in the reaction. In this case enrichment of the copolymer in alkoxyl groups occurs to the greatest extent. Copolymers formed from methacrylic acid and butyl vinyl ether in various proportions contain relatively fewer alkoxyl groups than the above ethyl vinyl ether copolymer. On this basis we may judge the differing activities of ethyl vinyl and butyl vinyl ethers. The same relation is to be found for the results for the methacrylic acid contents of the copolymer.

It follows from Table 1 that the results for the titration of carboxyl groups and the calculated composition of the copolymer from the elementary analysis are in satisfactory agreement. An exception is formed by copolymers obtained from methacrylic acid and alkyl vinyl ether in the ratio 1:3. This may be explained on the assumption that the number of carboxyl groups in the copolymer is reduced either owing to their addition to alkyl vinyl ethers, or owing to initial reaction with alkyl vinyl ethers followed by copolymerization as acylals: in both cases the final copolymers will be the same. This suggestion is confirmed by the fact that hydrolysis of these copolymers and subsequent titration of carboxyl groups and acetaldehyde gives results closely consistent with these views. The hydrolysis proceeds as follows [8]:



(XII)

Determination of acetaldehyde iodometrically [9] gives the content of the corresponding vinyl ether in the original copolymer.

EXPERIMENTAL

The starting materials were methacrylic acid, ethyl vinyl ether, and butyl vinyl ether. Methacrylic acid having the following constants was used in all the experiments: b.p. 160°; n_D^{20} 1.4313; d_4^{20} 1.0153; acid number 650 (mg KOH).

The vinyl ethers were prepared by Favorsky and Shostakovsky's method [10] and were purified by Shostakovsky and Prilezhaeva's method [11]. The ethyl vinyl ether used had the following constants: b.p. 35.9°; n_D^{20} 1.3778; d_4^{20} 0.7533. The butyl vinyl ether used had the following constants: b.p. 93.5-93.7°; n_D^{20} 1.4027; d_4^{20} 0.7791. Freshly distilled monomers were always used for the polymerization.

The polymerization was carried out in presence of benzoyl peroxide, which was purified by dissolution in chloroform, filtration, and precipitation with methanol [12]. The reprecipitation was repeated twice, after which further treatment with methanol was given and the material was dried in a vacuum desiccator until volatile substances (methanol) had been completely removed. The polymers and copolymers were dissolved in methanol having b.p. 64-65° and n_D^{20} 1.3300. Precipitation of the macromolecular substances obtained was effected with benzene of b.p. 80-80.5° and n_D^{20} 1.5010.

Experimental Procedure. The conditions for the copolymerization of methacrylic acid and alkyl vinyl ethers were investigated in sealed glass tubes, which were heated at 60 ± 1° in a thermostat until highly viscous or solid polymers were formed. In order to determine the activity of the benzoyl peroxide and the tendency of the original components to undergo polymerization, control experiments were carried out with methacrylic acid and the alkyl vinyl ethers separately.

The copolymerization of methacrylic acid with alkyl vinyl ethers was carried out in various molar ratios. The amount of benzoyl peroxide was 0.2% of the total weight of monomers. It was further necessary to determine the solubilities of the macromolecular compounds obtained in water, methanol, benzene, acetone, and ether. The polymers and copolymers were precipitated from solution with a 30-fold volume of precipitant. After separation of the macromolecular compounds, the mixture was distilled and the weight and composition of the residue were determined.

The presence of the original monomers in the polymers and copolymers was checked by extracting them with benzene and then estimating the multiple bonds in the extract with the aid of an aqueous solution of bromine

[13]. The polymer or copolymer was then dried, ground, extracted in the cold with benzene, and again dried. The polymers were dried in a vacuum drier at 45-50°, first at 15-20 mm, and then at 3 mm.

In order to calculate the yields of macromolecular compounds, drying was performed accurately within ± 0.01 g; for microanalysis the samples were dried to constant weight accurate within ± 0.0001 g. After being dried, the polymer and copolymer samples were stored in a vacuum desiccator over freshly calcined calcium chloride.

The separation of copolymers from polymers was effected by the method of selective dissolution. The elementary analysis was performed by micro methods. Carboxyl groups were determined in copolymers by titration. An excess of titration alkali was run into the polymer or copolymer solution, and the mixture was heated for 3-4 hours; the excess of alkali was then titrated with acid [14]. The structures and compositions of the synthesized compounds were studied.

Control Investigations. In order to verify the ability of the monomers used to undergo free-radical polymerization, control experiments were always carried out.

1. A study of the behavior of methacrylic acid toward benzoyl peroxide was carried out by the above-described procedure. The duration of an experiment was about eight hours, i.e., until a solid polymer of methacrylic acid was obtained. This polymer dissolved in cold water, in hot water, and in methanol. Titration revealed the presence in the polymer of 95.5% free carboxyl groups.

2. The behavior of benzoyl peroxide toward the alkyl vinyl ethers was carried out by the above-described procedure. The sealed tubes containing the alkyl vinyl ether and benzoyl peroxide were kept in the thermostat for 80 hours. The contents of the tubes were then distilled: the fractions obtained were found to be the original alkyl vinyl ethers, and a small amount of resinified material remained at the bottom; it was insufficient for quantitative investigation.

Copolymerization of Methacrylic Acid and Ethyl Vinyl Ether. For the copolymerization, 7.2 g of methacrylic acid and 17.8 g of ethyl vinyl ether were taken. The tubes were heated for 72 hours. The macromolecular compound formed was highly viscous. At the end of the reaction the tubes were cooled to 0°. The copolymerization conditions and the purification of the products are described above. The yield of copolymer was 10.75 g.

The copolymer obtained was ground, and its solubility in cold and hot water was studied. It was found that the water filtered from the copolymer contained no products having COOH groups; this was confirmed by titration in presence of phenolphthalein. The copolymer was soluble in methanol and ethanol, but insoluble in benzene and ether. The solutions of the copolymer in methanol were clear and viscous. In order to determine whether 1-ethoxyethyl methacrylate units were present in the copolymer chain, the material was titrated iodometrically. Some acetaldehyde was found, thus indicating the presence of 1-ethoxyethyl methacrylate units in the chain.

In addition, the copolymerization of methacrylic acid with ethyl vinyl ether was carried out with the following molar ratios of monomers (Table 2), other conditions being the same.

TABLE 2

Molar Ratios and Yields in Copolymerization of Methacrylic Acid and Ethyl Vinyl Ether

Molar ratio		Duration of polymerization (hr)	Yield of polymer (% on acid taken)	Appearance of polymer in tube before treatment
$CH_2=C(CH_3)COOH$	$CH_2=CH(OC_2H_5)$			
1.0	–	7.5	90.2	White solid
0.75	0.25	7.0	105.4	White solid
0.50	0.50	80.0	120.0	Clear solid
0.25	0.75	72.0	150.0	Highly viscous, clear mass
–	1.0	80.0	–	Liquid

The copolymers produced from the monomers taken in various ratios were soluble in methanol and ethanol, but insoluble in benzene and ether. The differences in composition had a marked effect on the behavior

of the copolymers toward water.

Copolymerization of Methacrylic Acid and Butyl Vinyl Ether. In this series of experiments, 5.56 g (1 molecular proportion) of methacrylic acid and 19.44 g (3 molecular proportions) of butyl vinyl ether were used. The duration of the polymerization was 72 hours. When the polymerization was complete, the tubes were cooled to 0°. The copolymerization conditions and the method of purification are described above. After reprecipitation of the copolymers, solvent and precipitant were distilled off under reduced pressure.

The following products were identified: solvent, precipitant, butyl vinyl ether, and methacrylic acid. A liquid having the specific odor of an acylal remained at the bottom of the distilling flask; p-toluylenediamine was added to the residue, and distillation was continued. As a result of the further distillation, an insignificant amount of liquid having n_D^{20} 1.4250 [7] was collected, and in addition some polymer remained in the flask. This was dissolved in acetone and then titrated iodometrically. The presence of 40.1% of ether groups was established. After being purified, the copolymer was dried; yield 7.65 g.

The ground copolymer was insoluble in cold and in boiling water. After being boiled with the copolymer, the water was filtered off, and was found to give a coloration with 0.05 N caustic soda in presence of phenolphthalein. The copolymer gave a gel in methanol and was insoluble in benzene.

Apart from this series of experiments on the copolymerization of methacrylic acid with butyl vinyl ether, other experiments were performed at other molar ratios. The same procedure was used for the copolymerization and the purification of the copolymers. The monomer ratios, yields, and other details are given in Table 3.

TABLE 3
Molar Ratios and Yields in Copolymerization of Methacrylic Acid and Butyl Vinyl Ether

Molar ratio		Duration of polymerization (hr)	Yield of polymer (% on acid taken)	Appearance of polymer in tube before treatment
$CH_2=\underset{\displaystyle COOH}{\overset{\displaystyle CH_3}{\overset{|}{C}}}$	$CH_2=\underset{\displaystyle OC_4H_9}{CH}$			
1.0	—	7.5	90.2	White solid
0.75	0.25	72	106.6	White solid
0.50	0.50	72	108.2	White solid
0.25	0.75	72	137.6	Clear solid
—	1.0	72	0	Liquid

The copolymers obtained with other monomer ratios were insoluble in benzene. The third copolymer (Table 3) gave a gel, insoluble in water, in the cold or at the boil.

The second copolymer (Table 3) gave a clear solution in methanol. In hot and in cold water these copolymers partially dissolve or swell.

SUMMARY

1. The conditions for the copolymerization of methacrylic acid with alkyl vinyl ethers have been investigated, and a number of new copolymers have been synthesized.

2. It has been shown that the copolymerization processes of unsaturated compounds in which there are functional groups having mobile hydrogen are accompanied by a number of side reactions.

3. It has been shown that acylals are formed in the course of the copolymerization process.

4. It has been established that screening of the carboxyl groups of the original methacrylic acid can be effected either by reaction of the methacrylic acid with alkyl vinyl ethers, or by copolymerization with the latter, or by addition of alkyl vinyl ethers to carboxyl groups of the copolymer.

5. It has been shown that, when suitable mixtures of methacrylic acid and alkyl vinyl ether react in presence of benzoyl peroxide, polymerization and copolymerization processes may predominate over side reactions.

6. In the course of investigations of the copolymerization of methacrylic acid and alkyl vinyl ethers, it has been shown that new copolymers, having hydrophilic (COOH) and hydrophobic (OR) groups, are formed.

7. It has been established that under these conditions alkyl vinyl ethers do not polymerize in presence of benzoyl chloride.

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* See Consultants Bureau Translation, page 453.

IONIC POLYMERIZATION OF VINYL ETHERS

M. F. Shostakovsky, B. I. Mikhantyev, and N. N. Ovchinnikova

Vinyl ethers in presence of catalysts are converted into oily, highly viscous, or film-forming polymers. Suitable catalysts are halides [1], including hydrogen halides [2] and various salts: $SnCl_2$, $SnCl_4$, $AlCl_3$, etc. [3]. Boron trifluoride has been widely used abroad for this purpose, and Favorsky and Shostakovsky have introduced ferric chloride into scientific practice [3]: the polymerization of vinyl ethers is brought about by addition, in catalytic quantities, of an alcoholic solution of ferric chloride, the process being carried out at a temperature close to the boiling point of the monomer. Ethyl vinyl ether (b.p. 36°), for example, is polymerized at 35-41° [4], and butyl vinyl ether (b.p. 93-94°) at above 90° [5].

The ionic polymerization of vinyl ethers has been provided with a theoretical basis in Shostakovsky's oxonium theory [6]. The temperature is one of the principal factors determining the course of these processes in practice. The dissociation range of the oxonium complexes of a given alkyl vinyl ether corresponds approximately to the boiling point of the ether.

Descriptions of the preparation and properties of polymers of alkyl vinyl ethers are generally to be found in patent specifications, or they refer to isolated cases. In order to fill this notable gap, we have studied the polymerization of C_3–C_{12} alkyl vinyl ethers in presence of $FeCl_3$.

In the polymerization of vinyl ethers, the purity of the original monomers is of prime importance. The polymers and copolymers are of the highest molecular weight when they are obtained from ethers purified as follows: the crude ether is distilled, washed five times with water, dried with potassium carbonate, and distilled; it is finally treated with sodium and again distilled [7]. Aldehydes, ketones, alcohols, and other oxygen-containing compounds capable of forming peroxides retard polymerization [8]. Peroxides are formed also when alkyl vinyl ethers are kept: Shostakovsky and coworkers have established that freshly washed and distilled ethyl vinyl ether must be used for polymerization within three days [4].

Polymerization of alkyl vinyl ethers in presence of $FeCl_3$ generally proceeds at the boiling point of the monomers, or somewhat higher than this. This fact is explained by Shostakovsky by the decomposition of the vinyl ether-catalyst complex with formation of an active monomer molecule, which serves as an initiator of polymer chains.

Polymerization of vinyl ethers is carried out at ordinary pressure. About one-tenth of the monomer to be polymerized is placed in a flask and heated to the boil; ferric chloride (5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol) is then added dropwise, and the temperature rises spontaneously by 3-5°, and the macromolecular product is formed at the high rate that is characteristic for ionic reactions. Termination of chains occurs on account of the addition of $\overline{O}R$ or $\overline{O}H$, or the elimination of a proton, at the end unit [9].

Lowering of the temperature below that recommended leads to the formation of polymers and copolymers of low viscosity. The temperature is maintained at the required level by heating or addition of catalyst. It should be noted that for monomers having more complex molecules it is better to maintain the temperature at 5-10° above the boiling point of the ether. The polymerization of isopentyl vinyl ether (b.p. 111°), for example, goes well at 120°. The more severe conditions required for the polymerization of this ether are evidently related to its lower activity and to the high stability of its complex (vinyl ether—$FeCl_3$).

The polymerization of 200-300 g of monomer requires 3-4 hours, and at the end of this period the still-warm product is treated in a vacuum (12-18 mm) at 80-150° for 5-6 hours, i.e., until constant weight and refractive index is attained. The yield is 70-90% of the theoretical value: the polymer generally contains about 1% of monomer, which can be determined quantitatively, and about 15% of monomer is lost during polymerization and treatment under vacuum.

Polymers of C_3-C_7 vinyl ethers are colorless, highly viscous substances. C_8-C_{12} vinyl ethers also form macromolecular compounds, but they are colorless-yellow in varying degree, which is to be explained by partial destruction of the polymers in the process of formation (150-200°). For purification purposes the polymers are dissolved in benzene or ether. The solution is filtered, and the polymer is precipitated from the filtrate with water or an alcohol having a smaller radical than that of the original monomer. Dissolution and precipitation of polymer is repeated 2-3 times, until it is completely clarified. Finally, the product is placed under vacuum in a boiling water bath until constant weight and refractive index is attained. In the course of the reprecipitation there is naturally some loss of polymer, which reduces the yield.

The polymers are soluble in ether, benzene, acetone, chloroform, and other solvents. The polymers are soluble also in the alcohols from which the monomers are prepared, and in higher alcohols. The characteristics of the vinyl ether polymers are given in the table. In the molecular-weight determination we used the constant 0.000534, as established by the Vinyl Compound Laboratory of the Inst. Org. Chem., Acad. Sci. USSR.

It follows from the table that the molecular refraction rises in regular fashion. The viscosity of a 0.1 M solution rises with increase in length of the polymer chain. Polymers obtained from ethers of normal structure have higher molecular weights than those obtained from ethers having a radical of iso structure.

EXPERIMENTAL

1. Polymerization of Methyl Vinyl Ether

The amount of methyl vinyl ether (b.p. 5.5°, n_D^0 1.3730; d_4^0 0.7725 [10]) taken was 58 g (1 mole). About one-tenth of this was placed in a flask cooled with ice water and provided with a reflux condenser, and one drop of catalyst (5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol) was added. After 15-20 minutes vigorous boiling set in: part of the ether then evaporated, and the remainder polymerized into a slightly yellow, highly viscous substance. A fresh portion of the ether was added to the polymer obtained. Polymerization occurred after 10-15 minutes, and the resulting polymer was less viscous than that obtained with addition of catalyst. As further portions of the ether and the catalyst were added, the process went with spontaneous rise in temperature to 30°, reaction being less vigorous than in the formation of the first portion of polymer. The yield of crude polymer was 39.5 g (68%); n_D^{20} 1.4515. In order to remove monomer, the crude polymer was heated at 14-18 mm in a boiling water bath to constant weight (one hour). After the vacuum treatment the polymer had the following constants: n_D^{20} 1.4640; d_4^{20} 0.9423; absolute viscosity 0.7125 centipoise; relative viscosity 1.1107; specific viscosity 0.0788; M 2545; yield 30.6 g (52%).

	Found %:	C 62.13; 62.06; H 9.79; 9.52
C_3H_6O.	Calculated %:	C 62.04; H 10.41

The polymer of methyl vinyl ether slowly dissolves in cold water, but is again precipitated when the solution is warmed. It is soluble in methyl and other alcohols, and also in the usual organic solvents.

2. Polymerization of Propyl Vinyl Ether

The amount of propyl vinyl ether (b.p. 65.1°, n_D^{20} 1.3922; d_4^{20} 0.7678 [9]) taken was 86 g (1 mole). About one-tenth of this was placed in a three-necked flask provided with mercury-sealed stirrer, reflux condenser, and thermometer with its bulb at the bottom of the flask. Catalyst (two drops) was added to the boiling ether, and the temperature rose to 70°, the mixture becoming thick. The whole of the monomer was added over a period of one hour (five portions at ten-minute intervals). The optimum temperature for the polymerization of propyl vinyl ether is 65-70°, and it may be maintained in two ways: by placing the flask in a warm bath, or by addition of catalyst to the mixture. The yield of crude polymer was 77.5 g (90%); n_D^{20} 1.4468.

The crude polymer was dissolved in 300 ml of benzene, and the solution obtained was filtered. Methanol (200 ml) was then added to the filtrate in order to precipitate the polymer. The lower layer was separated, and the solvent was driven off. The polymer was exposed to a vacuum (13-18 mm) in a boiling water bath until constant weight was attained. The material purified in this way (62 g, i.e., 72%) had the following characteristics: n_D^{20} 1.4528; d_4^{20} 0.9368; absolute viscosity 0.8010 centipoise, relative viscosity 1.2382, specific viscosity 0.2218; M 4830. The polymer is soluble in propyl and higher alcohols, and in a wide range of other organic solvents.

	Found %:	C 69.91; 69.63; H 12.12; 12.11
$C_5H_{10}O$.	Calculated %:	C 69.72; H 11.70

3. Polymerization of Isopropyl Vinyl Ether

The amount of isopropyl vinyl ether (b.p. 55-55.6°, n_D^{20} 1.3861; d_4^{20} 0.7520 [9]) taken was 86 g (1 mole). The polymerization and treatment of the crude polymer were carried out as in Expt. 2. The pure polymer (60.3 g, i.e.,

TABLE

Characteristics of Vinyl Ether Polymers *

Name of polymer	Yield (%)	d_4^{20}	n_D^{20}	Viscosity of 0.1 M (calculated on monomer) benzene solution at 20° (centipoise)			M, calculated for monomer	Degree of polymerization
				Absolute	Relative	Specific		
Poly(methyl vinyl ether)	68	0.9423	1.4640	0.7185	1.1107	0.0788	58 2545	44
Poly(ethyl vinyl ether) [4]	79	0.9570	1.4520	0.8015	1.2389	0.2051	72 5334	74
Poly(propyl vinyl ether)	90	0.9368	1.4528	0.8010	1.2382	0.2218	86 4830	56
Poly(isopropyl vinyl ether)	61	0.9268	1.4520	0.7986	1.2345	0.2103	86 4580	53
Poly(butyl vinyl ether) [12]	92	0.9280	1.4570	0.8040	1.2420	0.2544	100 4738	47
Poly(isobutyl vinyl ether) [3]	90	0.9265	1.4565	0.7978	1.2333	0.2234	100 4183	42
Poly(isopentyl vinyl ether) [13]	86	0.9117	1.4607	0.7946	1.2129	0.2464	114 4048	36
Poly(hexyl vinyl ether)	89	0.9126	1.4632	0.8034	1.2419	0.2736	128 4003	31
Poly(cyclohexyl vinyl ether)	92	0.9364	1.4894	0.7357	1.1373	0.1040	126 1545	12
Poly(heptyl vinyl ether)	89	0.9132	1.4651	0.8255	1.2761	0.2350	142 3099	29
Poly(octyl vinyl ether) [14]	89	0.9230	1.4667	0.8534	1.3192	0.3550	156 4262	27
Poly(isooctyl vinyl ether)	93	0.9097	1.4664	0.8368	1.2905	0.2717	156 3261	21
Poly(nonyl vinyl ether)	87	0.9118	1.4676	0.8957	1.3846	0.3449	170 3799	22
Poly(decyl vinyl ether)	80	0.9282	1.4682	1.0105	1.5620	0.5174	184 5488	30

70%) had the following constants: n_D^{20} 1.4520; d_4^{20} 0.9268; absolute viscosity 0.7986 centipoise, relative viscosity 1.2345, specific viscosity 0.2103; M 4580. With respect to solubility the polymer of isopropyl vinyl ether was similar to that of propyl vinyl ether.

Found %: C 69.94; 69.71; H 11.95; 11.87

$C_5H_{10}O$. Calculated %: C 69.72; H 11.70

4. Polymerization of Hexyl Vinyl Ether

The amount of hexyl vinyl ether (b.p. 143.5°, n_D^{20} 1.4168; d_D^{20} 0.7970 [11]) taken was 128 g (1 mole). The polymerization was carried out as in Expt. 2. The optimum temperature for the process is 145-150°. The yield of crude polymer was 114 g (89%); n_D^{20} 1.4580. The crude polymer was dissolved in 500 ml of benzene, the solution was filtered, and the polymer was reprecipitated with 250 ml of ethanol. The alcohol and benzene were driven off, and the polymer was exposed to a vacuum (1 mm) in a boiling water bath until constant weight was attained (two hours). After purification the product (78.1 g, i.e., 61%) had the following characteristics: n_D^{20} 1.4632; d_4^{20} 0.9126; absolute viscosity 0.8034 centipoise, relative viscosity 1.2419, specific viscosity 0.2736; M 4003. The polymer of hexyl vinyl ether is soluble in hexyl and higher alcohols, and also in benzene, ether, and other organic solvents.

Found %: C 74.69; 74.85; H 12.70; 12.53

$C_8H_{16}O$. Calculated %: C 74.94; H 12.58

*For all of the polymers the constants are ours.

5. Polymerization of Decyl Vinyl Ether

The amount of decyl vinyl ether (b.p. 224-225°, n_D^{20} 1.4347; d_4^{20} 0.8123 [11]) taken was 184 g (1 mole). The polymerization was carried out as in Expt. 2, the optimum temperature being 230-235°. The crude polymer was dissolved in benzene and precipitated with ethanol, and this reprecipitation operation was repeated twice The purified product (92.2 g, i.e., 50%) had the following constants: n_D^{20} 1.4682; d_4^{20} 0.9282; absolute viscosity 1.0105, relative viscosity 1.5620, specific viscosity 0.5174; M 5488. The polymer of decyl vinyl ether is soluble in decyl alcohol, benzene, and ether.

	Found %:	C 78.40; 78.49; H 12.75; 12.95
$C_{12}H_{24}O$.	Calculated %:	C 78.19; H 13.13

SUMMARY

1. The polymerization of C_3-C_{12} alkyl vinyl ethers had been studied.

2. The polymers obtained have been characterized with respect to viscosity, molecular weight, solubility, and elementary composition.

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* See Consultants Bureau Translation, page 105.
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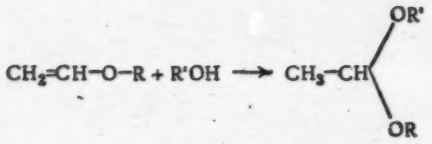
DERIVATIVES OF TERTIARY UNSATURATED ALCOHOLS

COMMUNICATION 1. SYNTHESIS OF ACETYLENIC ACETALS FROM VINYL ETHERS AND ACETYLENIC ALCOHOLS

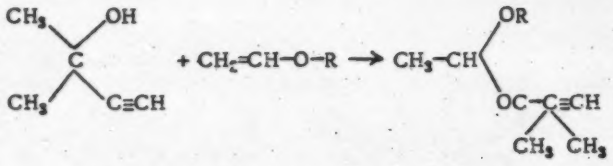
M. F. Shostakovsky and I. A. Shikhiev

At the present time the study of acetals derived from saturated and unsaturated alcohols presents great theoretical interest [1]. These compounds are highly reactive owing to the presence in them of a number of reaction centers. As the investigations of Shostakovsky and co-workers have shown [2], the simplest method of preparing acetals is by the addition of various alcohols to vinyl ethers in the manner indicated in the following equation:



(1)

The present investigation is concerned with the synthesis of acetylenic acetals, the formation of which may be represented by the following equation:



(2)

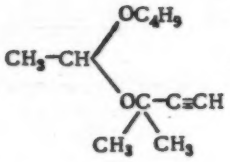
in which R = C_2H_5; i-C_3H_7; i-C_4H_9; C_4H_9

(I) (II) (III) (IV)

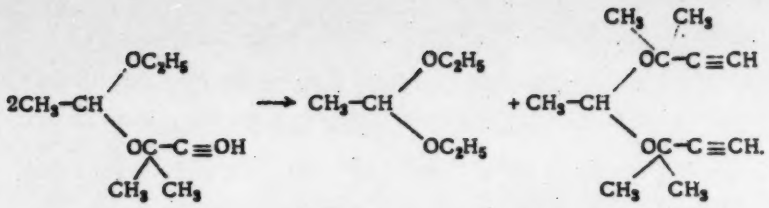
The addition of primary, secondary, and tertiary alcohols, and also of the corresponding unsaturated alcohols, to vinyl ethers, although performed by the same method in all cases, varies with respect to the experimental conditions required in the reaction.

We find, on passing from saturated alcohols (1) to unsaturated alcohols (2), that the acetals obtained are of still higher reactivity. The synthesis of acetals of the acetylenic series is best effected under mild conditions, i.e., in presence of catalyst at moderate temperature. The corresponding synthesis with heating in absence of catalyst is not applicable in this case [3].

In one of their papers Shostakovsky and Gershtein [4] have described the synthesis of an acetylenic acetal of the following structure:



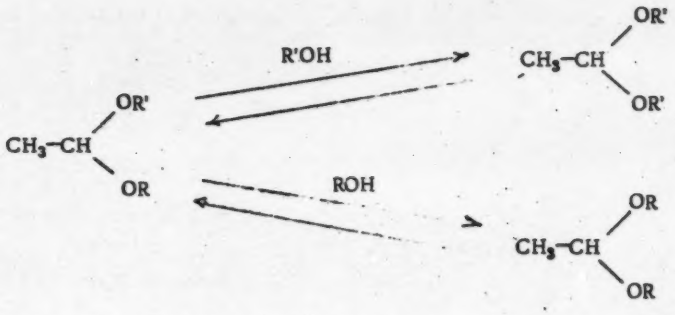
Since no disproportionation products were obtained in the course of the preparation of the acetal IV, it may be assumed that acetals of this series are not capable of disproportionation. We have, however, established that acetals derived from tertiary acetylenic alcohols undergo disproportionation to an extent that depends on the nature of the other alcohol residue. The disproportionation of mixed acetylenic acetals proceeds according to the equation:



(VI) (V)

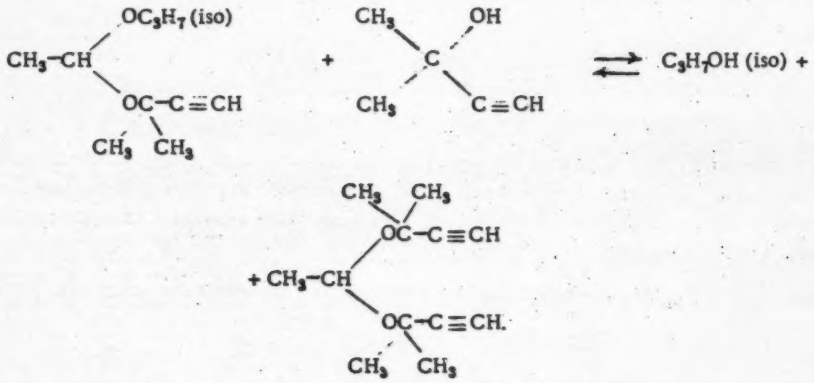
In the course of the synthesis of acetals of this series it was established that the tendency to undergo disproportionation falls off, according to the nature of the second residue, in the following order: $OCH_3 > OC_2H_5 > OC_3H_7 > OC_4H_9$. It may, therefore, be supposed that disproportionation depends to a certain extent on the size of the radical.

It is known [2, 5] that, under suitable conditions, saturated acetals undergo alcoholysis in an alcoholic medium according to the equations:

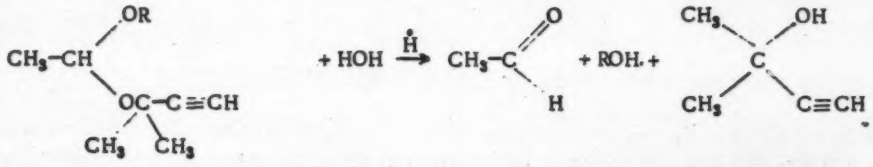


These equations indicate new synthetic methods for passing from unsymmetrical to symmetrical acetals, and in the reverse direction. As regards acetals derived from tertiary acetylenic alcohols, they also are able to undergo alcoholysis.

We have shown that the alcoholysis of acetaldehyde isopropyl 1,1-dimethyl-2-propynyl acetal in a medium of the acetylenic alcohol proceeds according to the equation:



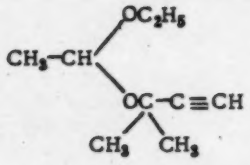
Altogether, we have prepared the ethyl, isopropyl, isobutyl, and butyl 1,1-dimethyl-2-propynyl acetals. Their structures were verified by breaking them down hydrolytically into their components as indicated in the equation:



EXPERIMENTAL*

The following starting materials were employed: 1,1-dimethyl-2-propyn-1-ol, b.p. 101-103°; n_D^{20} 1.4202; d_4^{20} 0.8578; ethyl vinyl ether, b.p. 36.0°; n_D^{20} 1.3776; d_4^{20} 0.7730; isopropyl vinyl ether, b.p. 55-55.5°; n_D^{20} 1.3860; d_4^{20} 0.7518; isobutyl vinyl ether, b.p. 83-83.5°; n_D^{20} 1.3986; d_4^{20} 0.7680; butyl vinyl ether, b.p. 93-94°; n_D^{20} 1.4020; d_4^{20} 0.7790.

1. Synthesis of the Ethyl 1,1-Dimethyl-2-propynyl Acetal I



A mixture of 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol and 72 g (1 mole) of ethyl vinyl ether was placed in a flask fitted with thermometer, condenser, and mechanical stirrer. The vinyl ether was taken in excess in order that no unchanged acetylenic alcohol should remain in the reaction mixture. Heating of the mixture for 18 hours at 80-90° did not result in acetal formation. When an addition of 0.02 ml of 30% hydrochloric acid was made to the mixture, the temperature rose to 57°. The mixture was set aside overnight, and on the next day the contents of the flask had become yellow. The reaction mixture was dried with potassium carbonate. The product (109 g) was vacuum-fractionated: unchanged starting materials were collected in a trap cooled to −16°, and the following fractions were collected:

Fraction I, b.p. 24-28° (12 mm); 4.6 g; n_D^{20} 1.4184
Fraction II, b.p. 42-43° (11-12 mm); 62 g; n_D^{20} 1.4162 (79.5%)
Undistilled residue 2.5 g

The contents of the trap (38 g) consisted essentially of unchanged ethyl vinyl ether containing traces of the acetylenic alcohol.

Investigation of Fraction II: d_4^{20} 0.8701; n_D^{20} 1.4162; found MR 45.01; calculated MR for $C_9H_{16}O_2$ 45.046; found M 147.3; 149.0; calculated M 156.

	Found %:	C 69.55; 69.83; H 10.28; 10.27
$C_9H_{16}O_2$	Calculated %:	C 69.23; H 10.25

These figures correspond to the unsymmetrical acetylenic acetal I. With ammoniacal silver nitrate Fraction II gave the white precipitate characteristic for monosubstituted acetylene compounds.

Hydrolysis of the Mixed Acetal I. A weighed amount of the acetal was placed in a flask, 25 ml of 2% sulfuric acid and 25 ml of 0.2 N sodium bisulfite were added, and the flask was shaken until the acetal had completely dissolved. After 20 minutes the excess of sodium bisulfite was titrated with 0.1 N iodine.

Found: 98.36% and 94.4% of theoretical amount of acetaldehyde.

Distillation of the reaction product at atmospheric pressure yielded the following fractions:

Fraction I, b.p. 32-41°; 32 g; n_D^{20} 1.3789
Fraction II, b.p. 95-108°; 17 g; n_D^{20} 1.4088
Undistilled residue 58 g

Fraction I consisted essentially of ethyl vinyl ether. Fraction II was treated twice with sodium and, on being redistilled, yielded a fraction (6 g) of b.p. 102-104°, n_D^{20} 1.3800; d_4^{20} 0.8275, and a resinous residue (6.5 g). The fraction of b.p. 102-104° corresponded to the symmetrical diethyl acetal, for which the literature gives [6]: b.p. 103-104°; d_4^{20} 0.8254; n_D^{20} 1.3820.

The residue from the first distillation (58g) was vacuum-distilled, yielding a fraction of b.p. 36-38° (10-11 mm) (46 g; n_D^{20} 1.4168; d_4^{20} 0.8710) and a slightly colored residue (7 g). The constants of the fraction of b.p. 36-38° corresponded to the above-described unsymmetrical acetylenic acetal (I); it gave the characteristic white precipitate with ammoniacal silver nitrate.

The residue from the vacuum distillation (7 g), a slightly colored, oily liquid, was distilled in a current of nitrogen, and yielded the fractions:

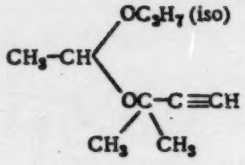
Fraction I, b.p. 67-78° (2 mm); 1.2 g; n_D^{20} 1.4422
Fraction II, b.p. 79-82° (2 mm); 3.6 g; n_D^{20} 1.4468 Residue 2 g (resinous)

* Senior laboratory worker Z. S. Volkova assisted in the experimental work.

Fraction II gave a characteristic voluminous white precipitate with ammoniacal silver nitrate and had d_4^{20} 0.8976; n_D^{20} 1.4468; found MR 57.72; calculated for $C_{12}H_{18}O_2$ F 2 MR 56.898. According to its constants, Fraction II corresponded to the symmetrical diacetylenic acetal V. This acetal changed color on standing.

The discrepancies in the constants must be explained by the purification difficulties and the comparatively low stabilities of the acetals.

2. Synthesis of the Isopropyl 1,1-Dimethyl-2-propynyl Acetal II



Hydrochloric acid (0.02 ml) was added to a mixture of 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol and 86 g (1 mole) of isopropyl vinyl ether, and the temperature of the reaction mixture rose to 78°. The mixture was set aside overnight, then dried with potassium carbonate, and finally vacuum-distilled through a trap cooled to −10-12°. The fractions obtained were:

Fraction I, b.p. 23-28° (11-12 mm); 9 g; n_D^{20} 1.3950
Fraction II, b.p. 47-48° (11-12 mm); (760 mm 153-55°); 65 g; n_D^{20} 1.4150 (76.5%)
Residue 2.3 g

The contents of the trap (47 g) consisted of isopropyl vinyl ether containing traces of 1,1-dimethyl-2-propyn-1-ol. Fraction I consisted essentially of isopropyl vinyl ether.

Investigation of Fraction II: d_4^{20} 0.8568; n_D^{20} 1.4150; found MR 49.57; calculated for $C_{10}H_{18}O_2$ F MR 49.644; found M 158.5; 161.0; calculated M 170.

Found %: C 70.18; 70.39; H 10.12; 9.89
$C_{10}H_{18}O_2$ Calculated %: C 70.59 H 10.59

Fraction II gave the characteristic white precipitate with an aqueous-alcoholic ammoniacal solution of silver nitrate, and it corresponded in its constants with the isopropyl 1,1-dimethyl-2-propynyl acetal II. It should be noted that in the vacuum distillation no disproportionation of the acetal was observed, whereas in distillation at atmospheric pressure some decomposition occurred. The acetal II was hydrolyzed under the same conditions as in the preceding experiment:

Found: 99.87% and 99.62% of theoretical amount of acetaldehyde

Alcoholysis of the Isopropyl 1,1-Dimethyl-2-propynyl Acetal. A sealed tube containing 42.5 g (0.25 mole) of the acetal and 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol was heated in an oil bath at 170-180° for 52 hours, and the reaction products were then vacuum-distilled through a trap cooled to −12-16°, the following fractions being collected:

Fraction I, b.p. 19-21° (12 mm); 8.6 g; n_D^{20} 1.4063
Fraction II, b.p. 28-69° (12 mm); 20.7 g; n_D^{20} 1.4219
Fraction III, b.p. 70-78° (12 mm); 46.4 g; n_D^{20} 1.4533
Residue 4.5 g (resinous)

The contents of the trap (3 g) were added to Fraction I and, after two distillations, 4.2 g of a product of b.p. 81-83°, n_D^{20} 1.3812; d_4^{20} 0.7870 was isolated. These constants correspond to isopropyl alcohol, for which the literature [7] gives: n_D^{20} 1.37757; b.p. 82-83°.

Fraction II gave the characteristic white precipitate with ammoniacal silver nitrate. A second fractionation of this fraction yielded 16 g of a product of b.p. 101-103° and d_{20}^{20} 0.8578, which correspond to 1,1-dimethyl-2-propyn-1-ol [1].

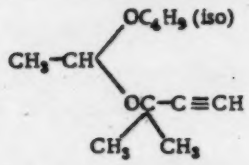
Fraction III was redistilled, when the greater part came over at 74-76° (12 mm), 32 g (33%) of a product corresponding to the symmetrical diacetylenic acetal V being obtained. Its constants were: n_D^{20} 1.4412; d_{20}^{20} 0.8967; found MR 57.15; calculated for $C_{12}H_{18}O_2$ F 2 MR 56.898.

Found %: C 74.12; 74.06; H 10.03; 10.12
$C_{12}H_{18}O_2$ Calculated %: C 74.22 H 9.27

The hydrolysis of the acetal obtained (V) was performed under the same conditions as in the preceding experiments:

Found: 98.39% and 98.10% of theoretical amount of acetaldehyde.

3. Synthesis of the Isobutyl 1,1-Dimethyl-2-propynyl Acetal III



The synthesis was performed under the same conditions as in the preceding experiments. Hydrochloric acid (0.02 ml) was added to a mixture of 42 g (0.5 mole) of 1,1-dimethyl-2-propyn-1-ol and 100 g (1 mole) of isobutyl vinyl ether, and the temperature of the mixture then rose to 80°. The reaction product was dried with potassium carbonate and vacuum-distilled through a trap cooled to −10-12°, the following fractions being collected:

Fraction I, b.p. 20-32° (9-10 mm); 8 g; n_D^{20} 1.4010
Fraction II, b.p. 55-56° (9-10 mm); 72 g; n_D^{20} 1.4170
Residue 3.6 g

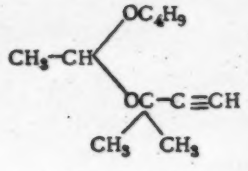
At atmospheric pressure the greater part of Fraction II came over at 173-174°. The yield was 78.26%. This fraction gave the white precipitate characteristic for monosubstituted acetylenes with aqueous-alcoholic ammoniacal silver nitrate, and it had the following constants: d_4^{20} 0.8587; n_D^{20} 1.4170; found MR 53.89; calculated for $C_{11}H_{20}O_2$ MR 54.282.

Found %: C 71.55; 71.55; H 10.90; 10.90
$C_{11}H_{20}O_2$. Calculated %: C 71.73; H 10.87

These figures correspond to the acetal III. The contents of the trap (55 g) consisted essentially of isobutyl vinyl ether containing traces of 1,1-dimethyl-2-propyn-1-ol. Hydrolysis of the acetal III was effected as in the preceding experiments:

Found: 96.58% and 100.3% of theoretical amount of acetaldehyde.

4. Synthesis of the Butyl 1,1-Dimethyl-2-propynyl Acetal IV



The synthesis was performed as in the preceding experiment and yielded 75 g (81.52%) of a product having the following constants: b.p. 181-182° (760 mm); 62-63° (10-11 mm); n_D^{20} 1.4182; d_4^{20} 0.8592; found MR 53.99; calculated for $C_{11}H_{20}O_2$ MR 54.282.

The product obtained (IV) gave the characteristic white precipitate with an aqueous-alcoholic ammoniacal solution of silver nitrate.

For the acetal IV the literature [3] gives: b.p. 181-182°; d_4^{20} 0.8579; n_D^{20} 1.4190.

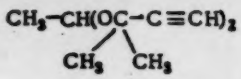
It should be noted that of the four unsymmetrical acetylenic acetals obtained, the butyl and isobutyl 1,1-dimethyl-2-propynyl acetals are the most stable when distilled. In this work we have shown also that the tertiary symmetrical unsaturated acetals V may be synthesized.

In the synthesis of the acetal I, disproportionation of the unsymmetrical acetylenic acetal was observed, the diethyl acetal VI and the diacetylenic acetal V being formed. The structure of the acetal V is proved by its synthesis by the alcoholysis of the isopropyl 1,1-dimethyl-2-propynyl acetal II in a medium of 1,1-dimethyl-2-propyn-1-ol.

SUMMARY

1. The ethyl, isopropyl, isobutyl, and butyl 1,1-dimethyl-2-propynyl acetals of acetaldehyde have been prepared. The last has been described in the literature, but the first three are now synthesized for the first time.

2. The possibility of synthesizing the symmetrical acetylenic acetal



has been demonstrated for the first time.

3. The structures of the acetals obtained have been proved by hydrolytic breakdown into their components.

4. The disproportionation of unsymmetrical acetylenic acetals has been demonstrated for the first time.

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Institute of Organic Chemistry
of the USSR Academy of Sciences

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* See Consultants Bureau Translation, page 57.

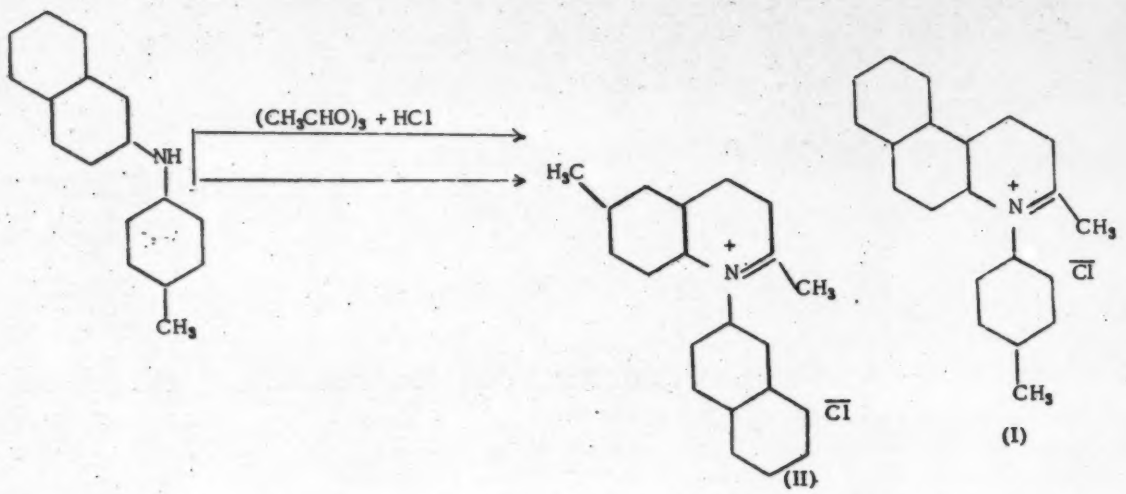
CYANINE DYES

COMMUNICATION 4. SYNTHESIS OF 3-METHYL-4-p-TOLYLBENZO[f]QUINOLINIUM IODIDE, AND SOME OF ITS REACTIONS

G. T. Pilyugin

The preparation and reactions of quaternary salts of nitrogenous heterocyclic bases having aryl radicals on the hetero-nitrogen atom have received very little study. In 1936 Todd, Bergel, and Karimullah synthesized quaternary salts of the thiazole series arylated on the nitrogen by heating thioacetamides with chloroacetone [1]. Kiprianov and Ushenko have prepared quaternary salts having aryl radicals from benzothiazole derivatives [2]. 1-Arylquinolinium salts and their reactions are practically unknown. Pilyugin and Krainer prepared 2-methyl-1-phenylquinolinium perchlorate and converted it into carbocyanines of the quinoline series having phenyl on the hetero-nitrogen atom [3]; they showed that the introduction of phenyl in place of ethyl led to a bathochromic shift in the absorption maximum of 10 mμ.

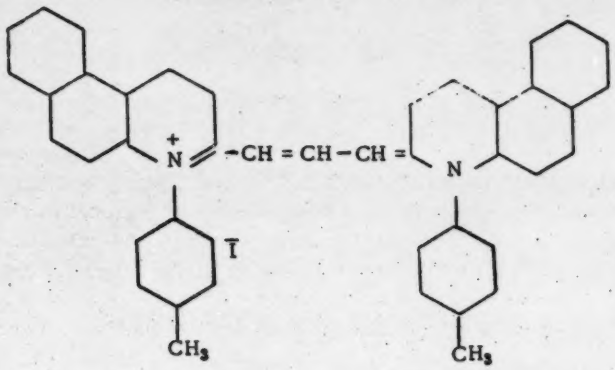
We have prepared a number of arylated quaternary salts derived from quinoline and have shown that the cyclization of secondary aromatic amines in presence of paraldehyde and a small amount of an aromatic nitro compound in an acid medium is a general phenomenon [4]. The systematic investigation of this question is of undoubted scientific interest. We have condensed N-p-tolyl-2-naphthylamine with paraldehyde in presence of hydrochloric acid, a reaction that could proceed in two directions with formation of the isomeric quaternary salts shown below:



Experiment showed, however, that under our conditions the cyclization led in the direction of the formation of the 3-methyl-4-p-tolylbenzo[f]quinolinium salt (I). No other reaction products were detected. The salt was isolated in a microcrystalline form and had a relatively sharp melting point (185-186°), which indicated that it was homogeneous. The value of the absorption maximum (644 mμ) of the trimethinecyanine dye prepared from it confirmed its structure; if it had had the other structure, 2,6-dimethyl-1-(2-naphthyl)quinolinium salt (II), the absorption maximum of the dye would have been at a considerably shorter wavelength, for the analogous carbocyanine with a 1-naphthyl radical has an absorption maximum of 622 mμ [5]. The structure of the

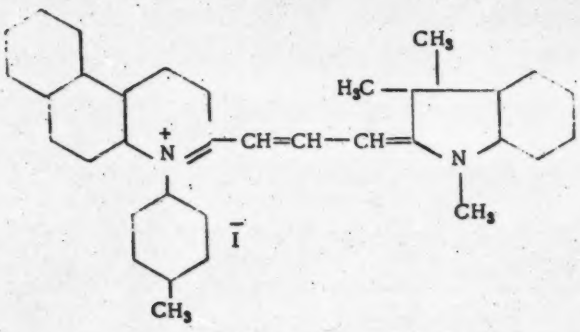
salt isolated is confirmed also by the fact that the absorption maximum of the dye obtained from the N-ethyl analog of this salt is 634 mμ [6].

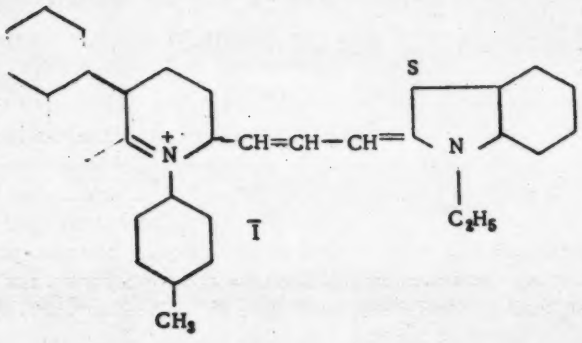
From the 3-methyl-4-p-tolylbenzo[f]quinolinium salts that we have synthesized for the first time we have prepared new cyanine dyes and have determined their absorption spectrum curves. Heating of the salt in pyridine with ethyl orthoformate yielded a dye of symmetrical structure, bis(4-p-tolyl-3-benzo[f]quinoline)trimethinecyanine iodide [7]



The absorption curve for this dye in ethanolic solution was determined on a spectrodensograph. Its absorption curve has two maxima at 644 and 595 mμ. The absorption maximum of this dye is displaced by 10 mμ toward the long waves with respect to that of its N-ethyl analog.

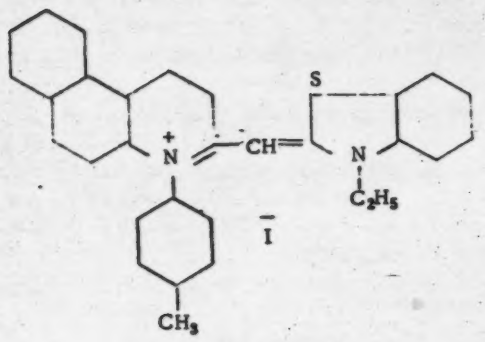
Condensation, in presence of pyridine and a few drops of acetic anhydride, of 3-methyl-4-p-tolylbenzo[f]-quinolinium iodide with 1,3,3-trimethyl-2-(2-N-phenylacetamidovinyl)pseudoindolium iodide and with 3-ethyl-2-(2-N-phenylacetamidovinyl)benzothiazolium iodide yielded unsymmetrical dyes [8]:





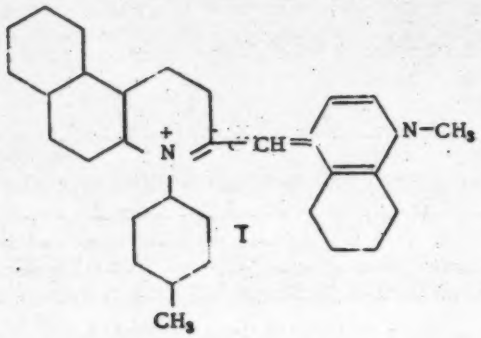
The absorption maxima of these unsymmetrical dyes are displaced from the additive value derived from the maxima of the corresponding symmetrical dyes in the direction of the ultraviolet, the first by 18.5 mμ, and the second by 5 mμ. The fused benzene ring at the f position in the quinoline nucleus displaces the absorption maxima of the unsymmetrical dyes by 4 and 8 mμ respectively with respect to the analogs without the fused benzene ring.

Condensation of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide with 3-ethyl-2-methylthiobenzothiazolium iodide yielded a dye of unsymmetrical structure, (4-p-tolyl-3-benzo[f]quinoline)(3-ethyl-2-benzothiazole)monomethinecyanine iodide:

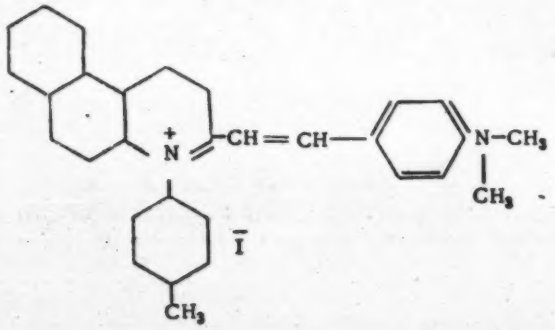


which has an absorption maximum at 495 mμ.

Heating of the quaternary salt with 1-methylquinolinium iodide in presence of caustic potash and sodium ethoxide yielded a monomethinecyanine of unsymmetrical structure [9]:



which has an absorption maximum in ethanol of 578 mμ. Condensation of the quaternary salt in pyridine with p-dimethylaminobenzaldehyde yielded the styryl derivative:



having an absorption maximum at 543 mμ.

EXPERIMENTAL

3-Methyl-4-p-tolylbenzo[f]quinolinium Iodide. N-p-Tolyl-2-naphthylamine (4 g), benzene (3 ml), and hydrochloric acid (sp. gr. 1.19; 1.8 ml) were introduced into a tube cooled in ice, and paraldehyde (2 ml) was added. The tube was sealed, and the contents were heated in a boiling water bath for 9-10 hours. The product of the condensation then had the appearance of a thick liquid, dark brown in color. The tube was opened, and the reaction mixture was treated several times with small portions of ether, which were stirred well with the reaction product, and then poured off. When the ether no longer became colored, the mass became very viscous. The crude quaternary chloride so obtained was dissolved in a small amount of alcohol and converted into the less soluble iodide by addition of 5 ml of a saturated solution of potassium iodide and heating for 5-6 minutes in a water bath. The mixture was cooled, and distilled water (50 ml) was added, when, in addition to the precipitated finely crystalline powder of quaternary salt, part of the product remained in the form of dark-brown viscous mass. The whole of the reaction product, in the form of a solution in aqueous alcohol, was heated at the boil for 30 minutes and then filtered hot. A yellow filtrate was obtained, and a small amount of semisolid resinous material remained on the filter. The filtrate was evaporated down on a water bath until an oily film formed on the surface; it was then set aside overnight to crystallize. The yellow crystalline precipitate was filtered off and washed with ether. The quaternary salt obtained melted at 185-186°. The semisolid mass that remained on the filter was dissolved in alcohol, a small amount of active charcoal was added to the solution, which was boiled for a few minutes and then filtered hot. On cooling, the solution yielded yellow crystals that melted at 187° and underwent the cyanine condensation in exactly the same way as the salt obtained from the first filtrate. The total yield of quaternary salt was 2.4 g (32%).

	Found %:	I 30.74
$C_{21}H_{18}NI$.	Calculated %:	I 30.82

Bis(4-p-tolyl-3-benzo[f]quinoline)trimethinecyanine Iodide. A mixture of 0.75 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.45 g of ethyl orthoformate, and 3 ml of pyridine was boiled in a small flask under reflux with continuous shaking for 25-30 minutes. As heating continued, the reaction mixture acquired a greenish color, which finally turned into an intense green. The solution was cooled, and the dye formed was precipitated with ether and dissolved in a small amount of alcohol. The alcoholic solution of dye was set aside overnight. On the next day the precipitated dye was filtered off and washed with small amounts of alcohol and ether. The dye, recrystallized from alcohol, formed dark-green crystals having a metallic reflex (0.27 g; 42.1%). It melted with decomposition at 225-227°. Its absorption maximum in ethanolic solution was 644 mμ.

	Found %:	I 17.76.
$C_{43}H_{33}N_2I$	Calculated %:	I 18.01.

(4-p-Tolyl-3-benzo[f]quinoline)(1,3,3-trimethyl-2-pseudoindole)trimethinecyanine Iodide. A mixture of 0.5 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.44 g of 1,3,3-trimethyl-2-(2-N-phenylacetamidovinyl)-pseudoindolium iodide, and 2 ml of pyridine was placed in a small flask fitted with reflux condenser and heated in a paraffin bath at 120-130° for 20-25 minutes. As heating proceeded the mass acquired a violet color, which became an intense bluish violet toward the end of the reaction. The mixture was cooled, and the dye was precipitated with ether and dissolved in 3 ml of alcohol; the solution was diluted with 5 ml of water and heated to the boil. On cooling, the aqueous-alcoholic mixture yielded dark-violet crystals of dye, which were filtered off and washed with ether. The dye was recrystallized from alcohol and was obtained as a crystalline powder having a greenish, metallic luster (0.21 g; 29.0%). It melted with decomposition at 243-245°. The absorption curve of the dye was determined in ethanolic solution on a spectrodensograph; the absorption maximum was 576 mμ.

	Found %:	I 21.10.
$C_{34}H_{31}N_2I$.	Calculated %:	I 21.35.

(4-p-Tolyl-3 benzo[f]quinoline)(3-ethyl-3-benzothiazole)trimethinecyanine Iodide. A mixture of 0.75 g of 3-methyl-4 p-tolylbenzo[f]quinolinium iodide, 0.55 g of 3-ethyl-2-(2-N-phenylacetamidovinyl)benzothiazolium iodide, and 4 ml of pyridine was placed in a small flask and heated in a paraffin bath at 130-135° for 20-25 minutes with frequent shaking. As heating progressed, the reaction mixture acquired a stable bluish-violet color. After cooling, the dye was treated with ether, which was mixed with the dye in successive portions, which were poured off. The mass of dye obtained was dissolved in a small amount of alcohol by application of heat, and then

reprecipitated with water; the dye was washed several times with water, until the water remained practically uncolored. The dye powder obtained was recrystallized from alcohol, yielding 0.29 g (35.4% calculated on the benzothiazole intermediate) of a dark-violet crystalline substance; m.p. 269-273° (dec.). Its absorption maximum was 596 mμ.

	Found %:	I 20.89
$C_{32}H_{27}N_2SI$	Calculated %:	I 21.20

(4-p-Tolyl-3-benzo[f]quinoline)(1-methyl-4-quinoline)monomethinecyanine Iodide•. A mixture of 0.5 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.26 g of 1-methylquinolinium iodide, 4 ml of absolute alcohol, and 0.5 ml of a saturated solution of sodium ethoxide was heated in a boiling water bath for 15 minutes with continual shaking. The reaction mixture was cooled and treated several times with ether (until it no longer became colored). The dye formed was dissolved by heating it with 6 ml of alcohol, and the solution was set aside overnight. On the next day the dye that had crystallized out was filtered off and washed with ether and a small amount of alcohol. It formed a violet crystalline powder, and its alcoholic solution was raspberry-colored. Recrystallization from alcohol yielded 0.28 g (39.80%) of the monocyanine, m.p. 204-205° (dec.). The absorption maximum was 578 mμ.

	Found %:	I 22.33
$C_{33}H_{27}N_2I$	Calculated %:	I 21.94

(4-p-Tolyl-3-benzo[f]quinoline)(3-ethyl-2-benzothiazole)monomethinecyanine Iodide. A mixture of 0.7 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.5 g of 3-ethyl-2-methylthiobenzothiazolium iodide, 8 ml of absolute alcohol, and 0.30 g of anhydrous sodium acetate was heated with continual shaking in a small flask fitted with reflux condenser for 15 minutes at 110-115° in a paraffin bath. The reaction mixture was cooled and treated with ether until a colored solution was no longer obtained. The residue was filtered off, and washed with ether and a small amount of alcohol. Recrystallization from alcohol yielded 0.53 g (54.37%) of a lemon-yellow crystalline powder, m.p. 221-224° (dec.). The alcoholic solution of the dye was light yellow. The absorption maximum of the dye in ethanolic solution was 495 mμ.

	Found %:	I 21.91
$C_{30}H_{25}N_2SI$	Calculated %:	I 22.17

3-(p-Dimethylaminostyryl)-4-p-tolylbenzo[f]quinolinium Iodide. A mixture of 0.5 g of 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, 0.2 g of p-dimethylaminobenzaldehyde, and 3 ml of pyridine was placed in a small flask attached to a reflux condenser and heated in a paraffin bath at 120-130° for 30-40 minutes. As heating proceeded, the reaction mixture acquired a crimson color, which became more intense toward the end of the heating. The dye formed, after cooling, was treated with ether, which was added, well mixed with the dye, and poured off, the treatment being repeated until the ether was no longer colored. The residue of dye was dissolved by heating with a small amount of alcohol, and the solution was set aside until the next day, when the precipitated dye was filtered off and washed with ether and a small amount of alcohol. The dye so obtained was in the form of green needles having a metallic luster; it gave a crimson solution in alcohol. After recrystallization from alcohol, the dye (45% yield) melted at 289-291° (dec.). Its absorption maximum was at 543 mμ.

	Found %:	I 23.18
$C_{36}H_{27}N_2I$	Calculated %:	I 23.40

SUMMARY

1. The quaternary salt 3-methyl-4-p-tolylbenzo[f]quinolinium iodide, which has not been described previously, has been synthesized by the cyclization of N-p-tolyl-2-naphthylamine.

2. From this quaternary salt the following six dyes have been synthesized (wavelength at absorption maximum given in parentheses): bis(4-p-tolyl-3-benzo[f]quinoline)trimethinecyanine iodide (644 mμ); (4-p-tolyl-3-benzo[f]quinoline)(1,3,3-trimethyl-2-pseudoindole)trimethinecyanine iodide (576 mμ); (4-p-tolyl-3-benzo[f]quinoline)(3-ethyl-2-benzothiazole)trimethinecyanine iodide (596 mμ); (4-p-tolyl-3-benzo[f]quinoline)(1-methyl-4-quinoline)monomethinecyanine iodide (578 mμ); (4-p-tolyl-3 benzo[f]quinoline)(3-ethyl-2-benzothiazole)monomethinecyanine iodide (495 mμ); and 3-(p-dimethylaminostyryl)-4-p-tolylbenzo[f]quinolinium iodide (543 mμ).

•In the Russian text, here and in the Summary, this dye is named as a 2-quinoline (not 4-quinoline) derivative. The name has been altered to conform with the formula given above and with the indications given in the reference [9] cited. — Publisher.

3. It has been shown that the presence of p-tolyl in place of ethyl on the hetero nitrogen atom of the benzo[f]quinolinium residue results in a bathochromic shift in the absorption maximum of the dye.

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* See Consultants Bureau Translation, page 347.
** " " " " " 491.

SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XXI. CONDENSATION

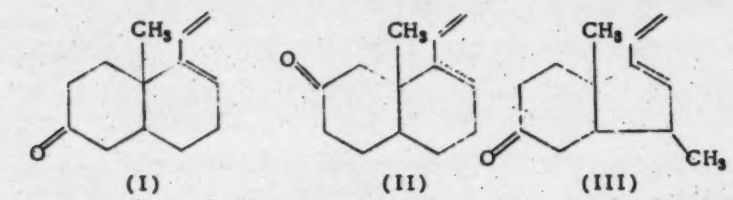
OF 3,4,4a,5,8,8a-HEXAHYDRO-8a-METHYL-1-VINYLNAPHTHALENE

WITH α,β-UNSATURATED CYCLIC KETONES.

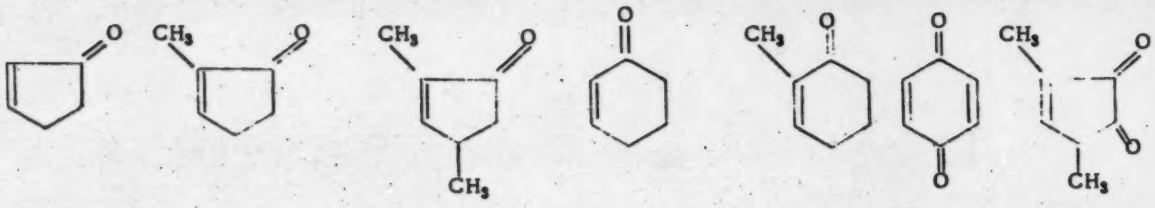
SYNTHESIS OF STEROID KETONES DERIVED FROM HYDROGENATED CYCLOPENTA[a]PHENANTHRENE AND CHRYSENE*

I. N. Nazarov, L. I. Shmonina, and I. V. Torgov

In previous communications we have described the synthesis of the bicyclic dienes, I, II, III, and IV, which react comparatively readily not only with citraconic and maleic anhydrides, but also with the α,β-unsaturated cyclic ketones VI – X and the diketones XI and XII [1]:



(I) (II) (III) (IV) (V)



(VI) (VII) (VIII) (IX) (X) (XI) (XII)

In this way we have succeeded in effecting for the first time the complete synthesis of numerous steroid ketones derived from hydrogenated cyclopenta[a]phenanthrene, chrysene, and benzofluorene, and having angular methyl groups.

The condensation of the bicyclic dienes I – IV with the α,β-unsaturated ketones VI – X generally resulted in the formation of a mixture of isomeric steroid ketones, differing, as we have shown [2], either in spatial configuration, or in the positions of the double bonds. The isomeric steroid ketones obtained by the condensation of the dienes I and II with 2-methyl-2-cyclopenten-1-one (VII) and 2,4-dimethyl-2-cyclopenten-1-one (VIII) have the

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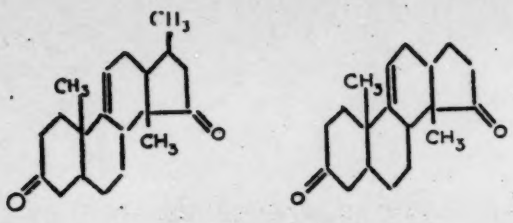
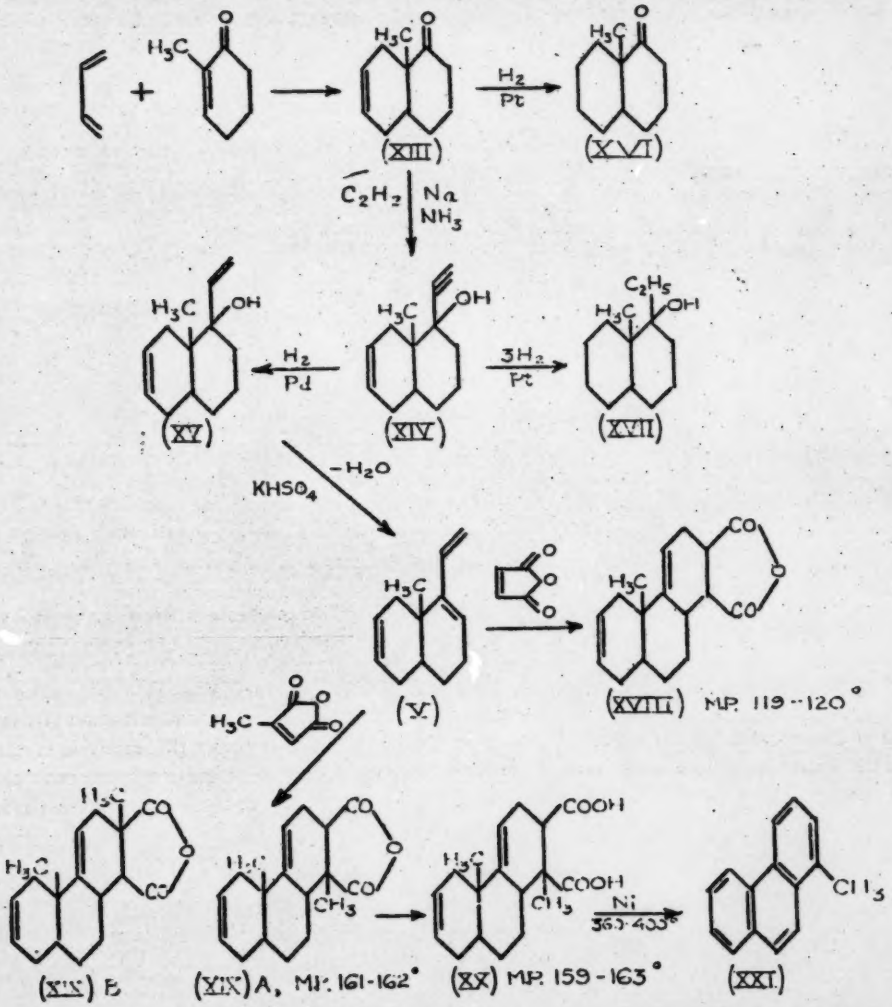
so-called "inverted" structure, i.e., have the keto group of ring D in position 15, as, for example:



The condensation of the bicyclic dienes I–IV with other α,β-unsaturated cyclic ketones probably proceeds in a similar way, i.e., in these cases also isomers having an "inverted" D ring will predominate.

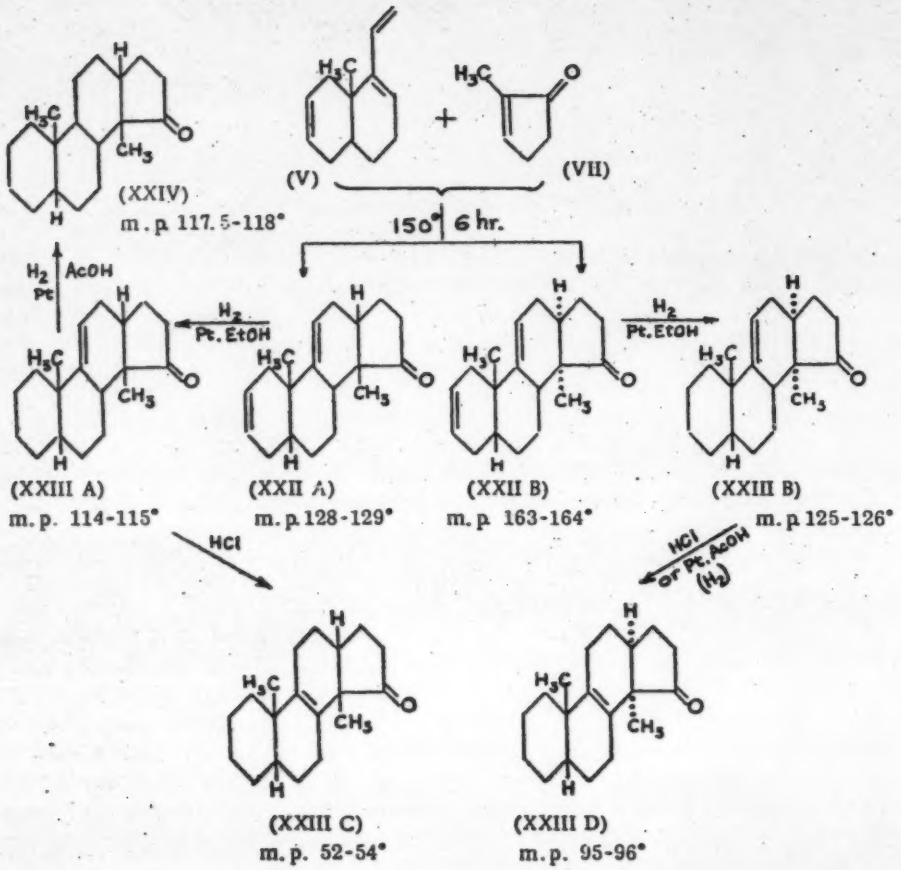
The present paper is devoted to an investigation of the condensation of the α,β-unsaturated cyclic ketones VII–XII with 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V), which was prepared similarly to the dienes I–IV by the route shown in the following scheme:



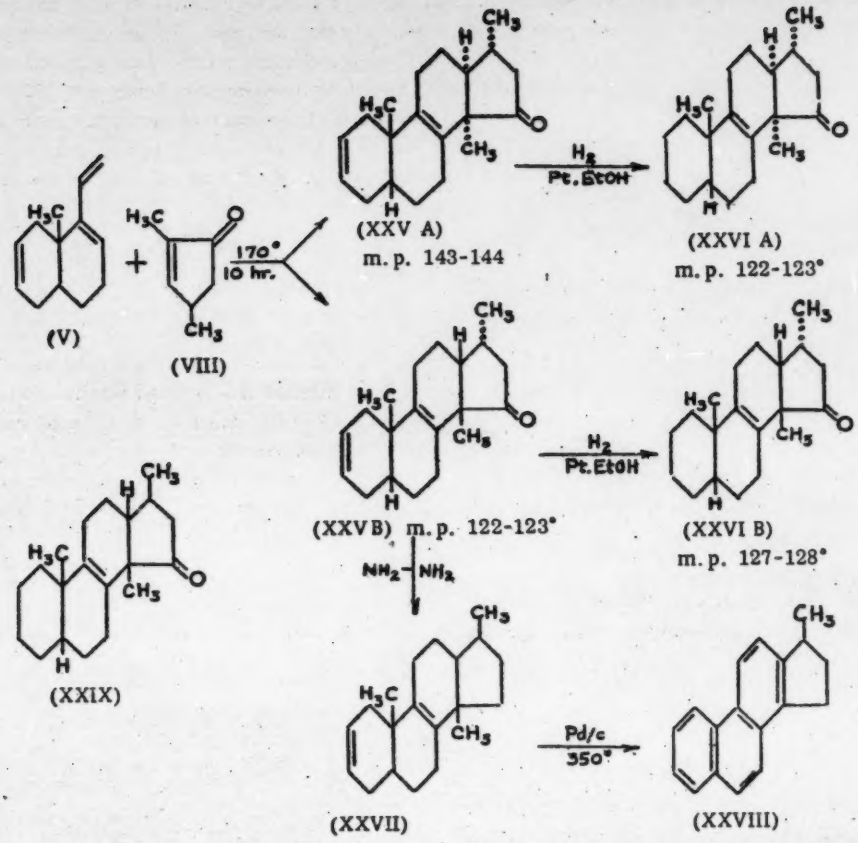
Heating of 1,3-butadiene with a four- or five-fold excess of 2-methyl-2-cyclohexen-1-one (X) in an autoclave at 245-250° for two hours yielded the previously described [1] cis-3,4,4a,5,8,8a-hexahydro-8a-methyl-1(2H)-naphthalenone (XIII), which, on being hydrogenated in presence of platinum, absorbed one molecule of hydrogen and formed cis-octahydro-8a-methyl-1(2H)-naphthalenone (XVI). When XIII was condensed with sodium acetylide in liquid ammonia, an 80% yield of 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV) was obtained; and selective hydrogenation of this over a palladium catalyst (1 molecule of hydrogen) yielded 1,2,3,4,4a,-5,8,8a-octahydro-8a-methyl-1-vinyl-1-naphthol (XV) quantitatively, whereas exhaustive hydrogenation (3 molecules of hydrogen) gave 1-ethyldecahydro-8a-methyl-1-naphthol (XVII). Dehydration of XV in a vacuum with the aid of finely ground, calcined potassium hydrogen sulfate at 130-140° gave a 70% yield of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V), which readily underwent diene condensation with the α,β-unsaturated cyclic ketones VII – XII, and also with maleic and citraconic anhydrides. It condensed with maleic anhydride even at room temperature with evolution of heat, yielding the crystalline anhydride of 1,2,3,4b,5,8,8a,9,10,-10a-decahydro-4b-methyl-1,2-phenanthrenedicarboxylic acid (XVIII).

The reaction between V and citraconic anhydride proceeds just as readily, yielding a mixture of crystalline isomers, probably having the structures XIX A and XIX B. From this mixture it was found possible to isolate the anhydride XIX A, which was hydrolyzed into the corresponding acid XX. The structure of this acid was proved by dehydrogenation in presence of Raney nickel in benzene at 360-400°, when 1-methylphenanthrene (XXI) was obtained. In this case it was not found possible to isolate the isomeric anhydride (XIX B), but its presence is confirmed by the analogous example of the condensation of citraconic anhydride with 1-vinyl-1-cyclohexene, which was performed recently in our laboratory: the two theoretically possible isomers were isolated.

Condensation of the hexahydromethylvinylnaphthalene V with 2-methyl-2-cyclopenten-1-one (VII) at 150° gave a 60% yield of a mixture of crystalline ketones, from which two isomers of 10,14-dimethyl-2,9-cardosteradien-15-one, XXII A and XXII B were isolated*. When these were hydrogenated in alcohol in presence of platinum,



*The steroid compounds are named according to Nazarov's nomenclature for synthetic steroids; see Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 726 (Consultants Bureau Translation, p. 651). — Publisher.

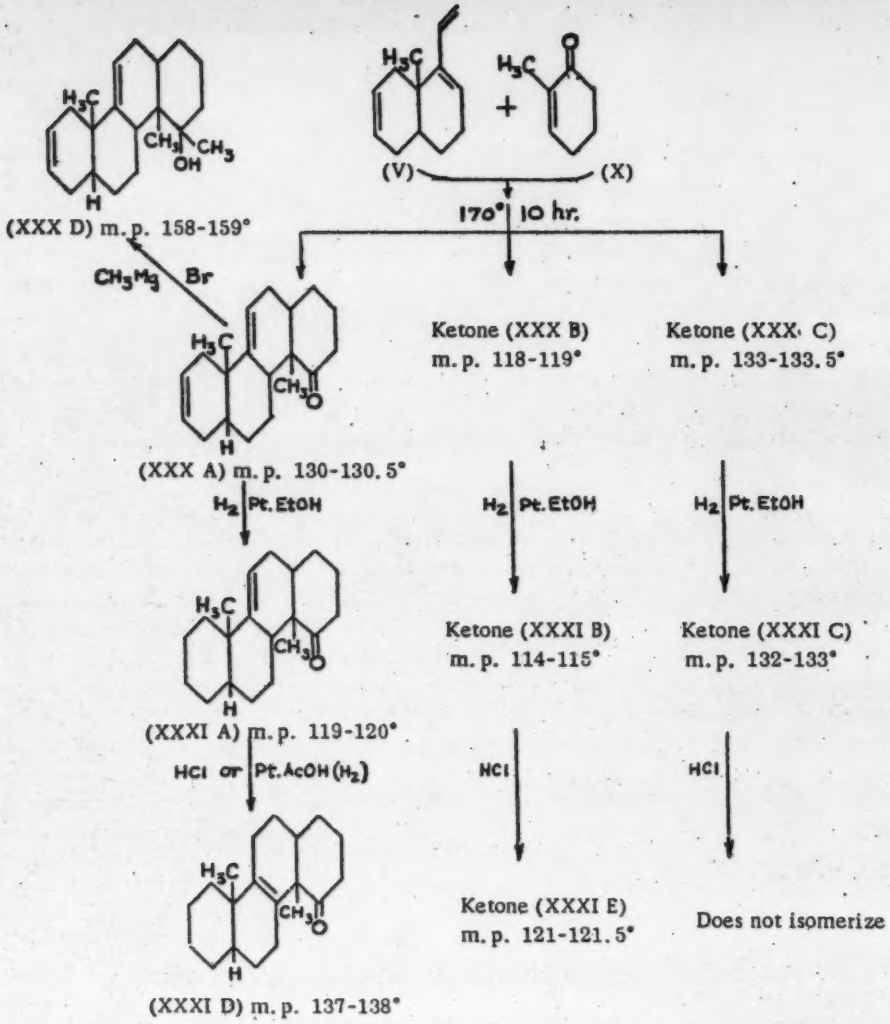


only one molecule of hydrogen was absorbed, i.e., the 9(11) double bond was not affected. The ketones (XXIII A and XXIII B) so obtained isomerized when boiled with hydrochloric and acetic acids with displacement of the double bond, yielding the ketones XXIII C and XXIII D, which were found to be identical with ketones obtained at the same time in our laboratory by another method; the structures of the latter have been proved [3]. This established also the structures of the ketones XXII A and XXII B (see the scheme on p. 957).

The ketone XXIII A, when hydrogenated over platinum in acetic acid, absorbed one molecule of hydrogen, yielding the fully saturated ketone XXIV. This is the first case in which the 9(11) double bond has been successfully hydrogenated in steroid ketones of this type. Under the same conditions, the ketones XXIII C and XXIII D were not hydrogenated at all, and the ketone XXIII B partially isomerized with displacement of the double bond, giving the ketone XXIII D.

Condensation of V with 2,4-dimethyl-2 cyclopenten-1-one (VIII) (at 170°) again resulted in the formation of two isomers, 10,14,17-trimethyl-2,9-cardosteradien-15-one (XXV A and XXV B). These, when hydrogenated over platinum, absorbed 1 molecule of hydrogen, giving the ketones XXVI A and XXVI B respectively. The ketone XXVI A was found to be identical with a ketone obtained at the same time in our laboratory by another method [2], and the structure of the latter was proved. The question of the structure of the original ketone (XXV A) was therefore solved. It is interesting to note that in this case, and, as we shall see below, also in the case of the ketone XXV B, the displacement of the double bond from the 9(11) to the 8(9) position occurs already in the course of the diene synthesis. We have found a similar case in the condensation of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (I) with 2-methyl-2 cyclohexen-1-one (X), and this is described in a previous communication [4].

As regards the ketone XXV B, we succeeded in converting it by a series of reactions into the so-called Diels hydrocarbon, 16,17-dihydro-17-methyl-15H-cyclopenta[a]phenanthrene (XXVIII): Kizhner reduction of the ketone



XXV B gave the hydrocarbon XXVII, which was dehydrogenated at 350° over palladized charcoal; the Diels hydrocarbon (XXVIII) was then isolated from the reaction mixture by chromatography. The melting points of the hydrocarbon and of its trinitrobenzene addition compound corresponded to the values given in the literature, and the respective mixed melting point tests gave no depression. The ketone XXV B, therefore, also has the "inverted" structure (see scheme on p. 958).

It must be pointed out that proof of the structures of the ketones XXVI by a second method that we have applied previously, namely oxidation of the D ring with an alkaline solution of iodide followed by dehydrogenation of the dicarboxylic acid formed into ethylmethylphenanthrene, was not found possible: in the oxidation iodine-containing products were obtained that were unsuitable for the subsequent dehydrogenation.

When heated with hydrochloric and acetic acids, neither of the ketones XXVI A and XXVI B changed. In a similar way, they were not hydrogenated in presence of platinum in acetic acid. These facts lead us to conclude that in these ketones, and therefore also in the ketones XXV A and XXV B, the double bond is not, as usual in the 9(11) position, but in the 8(9) position. Otherwise these ketones would have undergone isomerization. The displacement of the double bond evidently occurred in the course of the diene synthesis. The difference between the ketones XXV B and XXVI B and their isomers XXV A and XXVI A probably lies in the different spatial arrangement of the ($C_{13}-C_{14}$) substituents. The difference between the ketone XXVI B and the ketone XXIX previously obtained in our laboratory [2] is probably to be explained by a difference in the spatial configuration of the methyl at C_{17}.

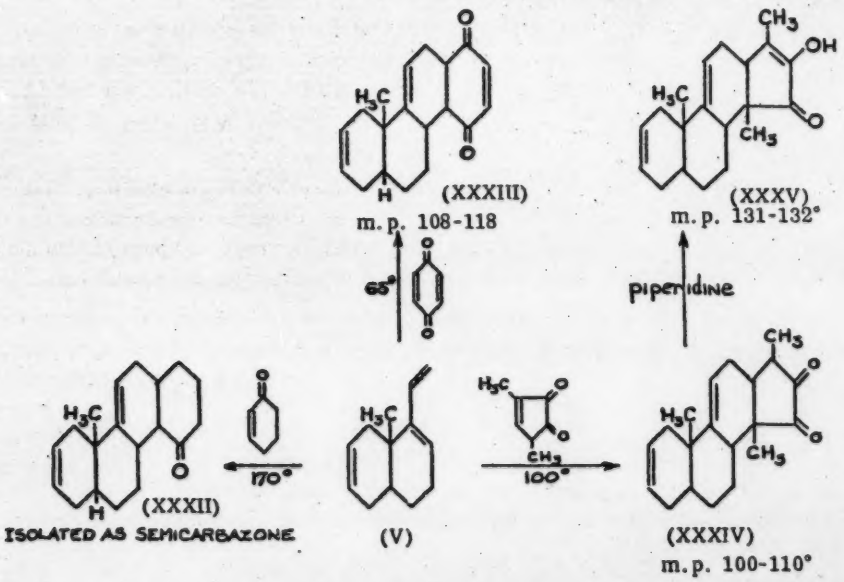
In the condensation of V with 2-methyl-2-cyclohexen-1-one (X) at 170°, it was found possible to isolate three isomeric ketones, XXX A, XXX B, and XXX C. When hydrogenated in alcohol in presence of platinum, each of the three isomers takes up one molecule of hydrogen, and the ketones XXXI A, XXXI B, and XXXI C, are obtained. On being boiled with hydrochloric and acetic acids, the first two ketones isomerize with displacement of the double bond, yielding the ketones XXXI D and XXXI E respectively.

The ketone XXXI D was found to be identical with a ketone prepared at the same time in our laboratory by another method [4]. The structures of the ketones XXX B and XXX C have not yet been elucidated.

When methylmagnesium bromide reacts with the ketone XXX A, the normal reaction occurs with formation of the tertiary alcohol XXX D. However, dehydration followed by dehydrogenation did not convert it into the expected 4-methylchrysene, but into chrysene itself (isolated in small amounts); i.e., a methyl group was eliminated in the dehydrogenation process.

None of the ketones XXXI A, XXXI B, and XXXI C are hydrogenated in acetic acid in presence of a platinum catalyst. It must be particularly noted that a double bond in the position 8(9) or 9(11) in steroid ketones is in general not readily hydrogenated. This fact is evidently associated with the spatial configurations of the ketones and the strong screening of the double bond. Incidentally, also the natural trans compounds, which have double bonds in the 7(8), 8(9), and 9(11) positions, are not hydrogenated under the usual conditions in presence of platinum or palladium; examples are Δ^{7}- and $\Delta^{8(9)}$-cholestenones [5].

When V was condensed with 2-cyclohexen-1-one (IX), the product was a noncrystallizing mixture of isomeric ketones, from which it was found possible to obtain a pure sample of the semicarbazone of XXXII (m.p. 237-237.5°). When V was condensed with p-benzoquinone (XI) at 65°, 10-methyl-2,9,16-cardochrysatriene-15,-17a-dione (XXXIII) was obtained in 30% yield. Condensation in a similar way of V with 3,5-dimethyl-3-cyclopentene-1,2-dione (XII) yielded 10,14,17-trimethyl-2,9-cardosteradiene-15,16-dione (XXXIV), which readily isomerized into the corresponding hydroxy ketone (XXXV) in presence of piperidine. We have observed such isomerizations previously. In conclusion it must be pointed out that dehydration of the octahydromethylvinylnaphthol XV must be carried out under strictly defined conditions, as otherwise the hexahydromethylvinylnaphthalene obtained (V) may be much contaminated by isomeric hydrocarbons that are unable to undergo the diene condensation even with maleic anhydride. It is this circumstance that explains the unsuccessful attempt of Butz [7] to condense the substance V with 2-methyl-2-cyclopenten-1-one (VII), for he chose an unsatisfactory method for the dehydration of the octahydromethylvinylnaphthol XV (he made use of phosphorus tribromide), and obtained a mixture of hydrocarbons that were inactive in the diene synthesis, the content of the hexahydromethylvinylnaphthalene V being negligible.



EXPERIMENTAL

2-Methyl-2-cyclohexen-1-one (X) [b.p. 66-67° (15 mm); n_D^{20} 1.4860], 2-cyclohexen-1-one (IX) [b.p. 83° (40 mm); n_D^{20} 1.4845], and 2-methyl-2-cyclopenten-1-one (VII) [b.p. 57° (15 mm); n_D^{20} 1.4778] were prepared by a method developed in our laboratory [8]. 2,4-Dimethyl-2-cyclopenten-1-one (VIII) [b.p. 164-165°; n_D^{20} 1.4672] was prepared by the cyclization of 2-methyl-1,5-hexadien-3-one [8]. 3,5-Dimethyl-3-cyclopentene-1,2-dione (XII) (m.p. 65-66°) was prepared by the oxidation of 2,4-dimethyl-2-cyclopenten-1-one with selenium dioxide [9]. Citraconic anhydride [b.p. 81° (2 mm); n_D^{20} 1.4710] was prepared by Shriner's method [16].

Condensation of 2-Methyl-2-cyclohexen-1-one (X) with 1,3-Butadiene. A mixture of 582 g of 2-methyl-2-cyclohexen-1-one (X), 75 g of 1,3-butadiene, and 2.5 g of diethylaniline was heated for two hours at 245-250° in a rotating stainless-steel autoclave. Vacuum distillation of the reaction mixture yielded 543 g of unchanged methylcyclohexenone and 26.5 g (45% on the ketone that had reacted) of a product of b.p. 93-95° (4 mm). In this way altogether 338 g of cis-3,4,4a,5,8,8a-hexahydro-8a-methyl-1(2H)-naphthalenone (XIII) was obtained as a fairly mobile liquid having a characteristic odor; b.p. 82-84° (2 mm); n_D^{20} 1.5050.

	Found %:	C 80.8; H 10.2
$C_{11}H_{16}O$.	Calculated %:	C 80.5; H 9.8

The semicarbazone melted at 225° with some decomposition (in a sealed capillary).

	Found %:	N 19.0; 18.95
$C_{12}H_{19}ON_3$.	Calculated %:	N 19.0

Butz [10] gives the following constants for cis-3,4,4a,5,8,8a-hexahydro-8a-methyl-1(2H)-naphthalenone: b.p. 67° at 0.5 mm; n_D^{20} 1.5042; and for the semicarbazone, m.p. 224.8-225°.

Hydrogenation of cis-3,4,4a,5,8,8a-Hexahydro-8a-methyl-1(2H)-naphthalenone (XIII). Some of the substance XIII (1.6 g) was hydrogenated in 5 ml of alcohol in presence of a platinum catalyst. Hydrogenation was continued for 40 minutes, and 245 ml of hydrogen (18°, 760 mm) was absorbed (theory requires 238 ml). Distillation yielded 1.3 g of cis-octahydro-8a-methyl-1(2H)-naphthalenone (XVI), b.p. 84-86° (3 mm); n_D^{20} 1.4950.

	Found %:	C 79.7; 79.7; H 10.8; 10.9
$C_{11}H_{18}O$.	Calculated %:	C 79.5; H 10.8

The dinitrophenylhydrazone recrystallized from methanol melted at 159-160°. The literature [11] gives for XVI itself b.p. 72-73° (0.8 mm); n_D^{20} 1.4895; and for its dinitrophenylhydrazone, m.p. 162.4-165.2°.

Condensation of cis-3,4,4a,5,8,8a-Hexahydro-8a-methyl-1(2H)-naphthalenone (XIII) with Acetylene. a) A solution of XIII (115 g) in 200 ml of absolute ether was placed in a three-necked flask fitted with mercury-sealed stirrer, dropping funnel, thermometer, and tube for passage of acetylene. The flask was cooled with a mixture of solid carbon dioxide and methanol (−70°), and the solution was saturated with acetylene for one hour (about 40 liters). Then, with continuous stirring and passage of acetylene, a suspension of potassium 1,1-dimethylpentyloxide (56 g of potassium was dissolved by heat in 350 ml of 2-methyl-2-hexanol) in 1 liter of absolute ether was added to the solution of ketone, and acetylene was passed (3-5 liters per hour) for a further 13 hours at −70°. The mixture was then set aside overnight, and on the next day acetylene was passed (3-5 liters per hour) for eight hours at −5°. The reaction mixture was decomposed with 150 ml of water, the ether layer was separated, and the aqueous layer was extracted with ether. The united ether extracts were neutralized with acetic acid and dried with sodium sulfate; the ether was driven off, and the residue was vacuum-fractionated, yielding 23 g of unchanged XIII and 80 g of 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV), a thick colorless liquid of characteristic odor, which gave a voluminous precipitate with an ammonical solution of silver oxide. The yield was 80% on the ketone that reacted; b.p. 98-99° (1.5 mm); n_D^{20} 1.5240.

	Found %:	C 82.3, 82.3; H 9.7, 9.5
$C_{13}H_{18}O$.	Calculated %:	C 82.1; H 9.5

Butz and coworkers [11] give the following constants for the tertiary alcohol XIV: b.p. 76-78° (0.3 mm); n_D^{20} 1.5275.

b) Liquid ammonia (1000 ml) was placed in the above-described flask, and with stirring at −70° sodium (38 g) was added in small pieces. The mixture was stirred for 20 minutes, and acetylene was then passed at 25-30 liters per hour for 3 hours 30 minutes. The rate of passage was then reduced to 15 liters per hour, and over a period of two hours a solution of 133 g of XIII in 150 ml of absolute ether was added. Passage of acetylene was continued

for a further 90 minutes at the same rate, and the mixture was then set aside at −70° overnight. On the next day stirring and passage of acetylene (15 liters per hour) were continued for two hours at −60°. The cooling bath was then removed, and when the temperature of the mixture rose to −35° the reaction mixture was decomposed by cautious addition of 150 g of ammonium chloride. When the ammonia had evaporated away and the temperature had risen to 0°, 200 ml of ether and 300 ml of water were added. The ether layer was separated, the aqueous layer was extracted with ether, and the united extracts were dried with sodium sulfate. The solvent was driven off, and the residue was vacuum-fractionated, yielding 125 g (86%) of 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV), b.p. 97-99° (2 mm); n_D^{20} 1.5245.

Exhaustive Hydrogenation of 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-naphthol (XIV). Some of the acetylenic alcohol XIV (1.5 g) was hydrogenated in 8 ml of alcohol in presence of a platinum catalyst. The amount of hydrogen absorbed was 587 ml (21°, 760 mm) (theory required 572 ml). The alcohol was driven off, and vacuum distillation of the residue yielded 1.2 g of 1-ethyldecahydro-8a-methyl-1-naphthol (XVII) as a thick colorless liquid of characteristic odor; b.p. 83-84° (0.05 mm); n_D^{20} 1.5060.

	Found %:	C 79.3, 79.3; H 12.3, 12.3
$C_{13}H_{24}O$.	Calculated %:	C 79.6; H 12.25

After standing for three months, the liquid partially crystallized. The crystals were washed with ether and then melted at 62-63°.

	Found %:	C 79.8, 79.65; H 12.3, 12.0
$C_{13}H_{24}O$.	Calculated %:	C 79.6; H 12.25

The ethyldecahydromethylnaphthol XVII was probably obtained in the form of two stereoisomers differing in the configuration at C_1. The original acetylenic alcohol XIV, therefore, must have been a mixture of stereoisomers differing in the configuration at C_1.

Preparation of 1,2,3,4,4a,5,8,8a-Octahydro-8a-methyl-1-vinyl-1-naphthol (XV). The acetylenic alcohol XIV (80 g) was hydrogenated in 100 ml of alcohol in presence of palladium on a calcium carbonate carrier. Hydrogenation was continued for 3 hours 30 minutes, and was interrupted when 9700 ml of hydrogen (21°, 760 mm) had been absorbed, since a test for a triple bond was negative (theory requires the absorption of 10,100 ml of hydrogen). After filtration and removal of alcohol, vacuum-distillation yielded 77 g of 1,2,3,4,4a,5,8,8a-octahydro-8a-methyl-1-vinyl-1-naphthol (XV) as a thick colorless liquid having a feeble odor; b.p. 91-93° (2 mm); n_D^{20} 1.5215.

	Found %:	C 81.2; H 10.4
$C_{13}H_{20}O$.	Calculated %:	C 81.25; H 10.4

Butz and coworkers [12] give the following constants for the tertiary alcohol XV: b.p. 76-80° (0.3 mm); n_D^{20} 1.5226.

Dehydration of 1,2,3,4,4a,5,8,8a-Octahydro-8a-methyl-1-vinyl-1-naphthol (XV). A mixture of 4.5 g of the ethylenic alcohol XV and 2.5 g of finely ground potassium hydrogen sulfate was heated at 130-140° for 30 minutes at reduced pressure (100-110 mm). The product was then distilled from the reaction mixture at 3 mm, dried with calcium chloride, and again distilled, yielding 3 g (75%) of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V), a slightly yellowish mobile liquid of characteristic odor; b.p. 74-74.5° (1 mm); n_D^{20} 1.5250.

	Found %:	C 89.4, 89.4; H 10.7, 10.5
$C_{13}H_{18}$.	Calculated %:	C 89.65; H 10.35

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with Maleic Anhydride. A mixture was made of 0.3 g of the hexahydromethylvinylnaphthalene and 0.17 g of maleic anhydride; there was noticeable evolution of heat. In order to complete the reaction, the mixture, diluted with 1 ml of absolute benzene, was heated in a sealed tube in a boiling water bath for three hours. When the benzene had evaporated away, the mass crystallized out. Two crystallizations from hexane gave the pure anhydride of 1,2,3,4b,5,8,8a,-9,10a-decahydro-4b-methyl-1,2 phenanthrenedicarboxylic acid (XVIII), m.p. 119-120° (in a sealed capillary).

	Found %:	C 75.15; H 7.4
$C_{17}H_{20}O_3$.	Calculated %:	C 75.00; H 7.4

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with Citraconic Anhydride. a) A mixture of 1.6 g of V and 1.2 g of citraconic anhydride in 2 ml of absolute benzene was left in a sealed tube at room temperature for one day and was then heated at 100° for seven hours. After removal of benzene the

residue crystallized out, yielding 0.8 g (30%) of a mixture of the anhydrides XIX A and XIX B, m.p. 133-145°, in which the anhydride XIX A predominated. Crystallization from hexane gave crystals of m.p. 135-150° (in a sealed capillary).

	Found %:	C 75.9; H 7.9
$C_{19}H_{22}O_3$.	Calculated %:	C 75.5; H 7.7

Further recrystallization from hexane yielded a small amount of pure crystals, m.p. 161-162° (in a sealed capillary).

	Found %:	C 75.6, 75.8; H 7.7, 7.8
$C_{19}H_{22}O_3$.	Calculated %:	C 75.5; H 7.7

b) A mixture of 6.5 g of V, 4.2 g of citraconic anhydride, and 3 ml of absolute benzene was left for two days in a sealed tube at room temperature. The mixture partially crystallized out, and 3.5 g of crystals, m.p. 120-135°, was separated. The liquid portion remaining after separation of the crystals was heated for six hours in a sealed tube in a boiling water bath. The liquid remaining after removal of benzene did not crystallize; citraconic anhydride (2 g) was added to it, and heating was continued for a further six hours at 125°. After removal of the excess of citraconic anhydride by distillation and treatment of the residue with absolute methanol, a further 0.3 g of crystals, m.p. 105-135°, was obtained (total yield 36%). Fractional crystallization from a mixture of hexane and benzene did not result in the isolation of a pure product. Mixtures of crystals of the following melting points were separated: 159-163°; 153-162°; 134-139° (in sealed capillaries).

Hydrolysis of the Anhydrides XIX A and XIX B. The crystalline mixture of anhydrides (0.3 g; m.p. 134-139°) was heated with 12 ml of 50% acetic acid for six hours at 90° and three hours at 103-105°. The crystals that came down on cooling were recrystallized from 50% acetic acid, and they melted at 159-163° (in a sealed capillary).

	Found %:	C 70.8, 70.95; H 8.1, 8.1
$C_{19}H_{24}O_4$.	Calculated %:	C 71.0; H 7.9

The crystalline mixtures of anhydrides of m.p. 159-163° and 153-162° were also hydrolyzed under the same conditions. In both cases crystals of an acid of m.p. 159-163° were isolated, and these gave no melting-point depression in admixture with the analyzed sample.

The fact that different mixtures of the anhydrides give the same substance when hydrolyzed evidently indicates that the corresponding acids have close melting points and identical solubility and are therefore not separated, but give a constant mixture of m.p. 159-163°.

Dehydrogenation and Decarboxylation of 1,2,3,4b,5,8,8a,9,10,10a-Decahydro-1,4a-dimethyl-1,2-phenanthrene dicarboxylic Acid (XX). The above-described acid (m.p. 159-163°) (0.7 g), 25 ml of dry benzene, and 3 g of nickel catalyst were heated in a 200-ml autoclave for 17 hours at 360-380°, 3 hours at 380-400°, and 3 hours 30 minutes at 400-410°. The residue after evaporation of the benzene consisted of 0.5 g of a dark-colored viscous mass, from which, after 10-12 hours, 100 mg of crude 1-methylphenanthrene crystals separated (XXI). Three crystallizations from methanol yielded 60 mg of crystals of m.p. 120-122° (in a sealed capillary).

	Found %:	C 93.55, 93.8; H 6.40, 6.5
$C_{15}H_{12}$.	Calculated %:	C 93.75; H 6.25

The picrate melted at 132° (from alcohol).

For 1-methylphenanthrene the literature gives m.p. 118° [13], 120-121° [14], and for the picrate: m.p. 135-136° [13], 139° [14].

2-Methylphenanthrene melts at 56-57°, and its picrate at 118-119° [15].

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-Methyl-2-cyclopenten-1-one (VII). A mixture of 10 g of the hexahydromethylvinylnaphthalene V and 20 g of the methylcyclopentenone VII was heated in a sealed tube in an atmosphere of carbon dioxide for six hours at 150°. The excess (17 g) of the methylcyclopentenone was distilled off under reduced pressure (15 mm), and the residue then crystallized out, yielding 8.6 g (55%) of a mixture of the isomeric steroid ketones XXII A and XXII B, m.p. 90-123°. By this method altogether 24 g of the mixture of isomers was obtained and then fractionally crystallized, yielding 6 g of ketone XXII A, m.p. 128-129° and 4 g of ketone XXII B, m.p. 163-164°.

Analysis of Ketone XXII A

	Found %:	C 84.3, 84.3; H 9.7, 9.8
$C_{19}H_{26}O$.	Calculated %:	C 84.4; H 9.6

Analysis of Ketone XXII B

	Found %:	C 84.1, 84.2; H 9.6, 9.7
$C_{19}H_{26}O$.	Calculated %:	C 84.4; H 9.6

Hydrogenation of Ketones XXII A and XXII B. The ketone XXII A of m.p. 128-129° (1.4 g) was hydrogenated in 40 ml of methanol in presence of an Adams platinum catalyst. Hydrogenation was complete in 90 minutes, the amount of hydrogen absorbed being 146 ml (26°, 755 mm) (128 ml theoretically required). The usual treatment and crystallization from methanol yielded 1.2 g of the ketone XXIII A, m.p. 114-115°.

	Found %:	C 84.0; H 10.4
$C_{19}H_{28}O$.	Calculated %:	C 83.8; H 10.3

In the same way, hydrogenation of 0.8 g of ketone XXII B of m.p. 163-164° yielded 0.7 g of the ketone XXIII B, m.p. 125-126°.

	Found %:	C 83.8; H 10.4
$C_{19}H_{28}O$.	Calculated %:	C 83.8; H 10.3

Hydrogenation of Ketone XXIII A. The ketone XXIII A of m.p. 114-115° (200 mg) was hydrogenated in 5 ml of acetic acid in presence of an Adams platinum catalyst (50 mg). The usual treatment and crystallization from petroleum ether yielded 55 mg of the ketone XXIV, m.p. 117.5-118°.

	Found %:	C 83.1, 83.2; H 11.3, 11.45
$C_{19}H_{30}O$.	Calculated %:	C 83.2; H 10.95

The melting point of the ketone obtained (XXIV) was depressed (to 106-110°) when mixed with the original ketone.

Isomerization of the Ketone XXIII A. A mixture of 0.7 g of ketone XXIII A, m.p. 114-115°, 13 ml of acetic acid, 11 ml of concentrated hydrochloric acid, and 15 ml of toluene was boiled under reflux for ten hours. The toluene layer was separated, neutralized by agitation with 5% caustic soda, filtered, and distilled to remove solvent. The residue was crystallized from petroleum ether, yielding 0.5 g of the ketone XXIII C, m.p. 52-54°. In admixture with the ketone obtained at the same time in our laboratory by another method [3] it showed no melting point depression. The ketone XXIII C did not undergo hydrogenation in acetic acid in presence of a platinum catalyst.

Isomerization of the Ketone XXIII B. a) The isomerization was effected in presence of hydrochloric acid, as described above; from 100 mg of ketone XXIII B, m.p. 125-126°, 30 mg of ketone XXIII D, m.p. 95-96° was obtained. In admixture with the ketone of m.p. 92-93° obtained at the same time in our laboratory by another method [3] it showed no melting point depression.

b) A mixture of 200 mg of the ketone XXIII B, m.p. 125-126°, and 5 ml of acetic acid was shaken in an atmosphere of hydrogen in presence of 50 mg of Adams platinum oxide for two hours. The usual treatment and crystallization from petroleum ether yielded 20 mg of the original ketone (m.p. 119-121°; satisfactory mixed m.p.) and 100 mg of ketone XXIII D, m.p. 92-93° (no depression in admixture with above-described sample of the ketone).

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2,4-Dimethyl-2-cyclopenten-1-one (VIII). A mixture 6 g of the triene V and 24 g of 2,4-dimethyl-2-cyclopenten-1-one (VIII) (b.p. 164-165°; n_D^{20} 1.4672) was heated for ten hours at 170° in a glass tube in an atmosphere of carbon dioxide. Excess (18 g) of the ketone was distilled off under reduced pressure (15 mm), and a mixture of petroleum ether and benzene (10 ml, 10:1) was added to the residue, when the mass partially crystallized out. Fractional crystallization from methanol yielded 1.3 g of ketone XXV A, m.p. 143-144°, and 1.6 g of ketone XXV B, m.p. 122-123°

Analysis of the Ketone XXV A

	Found %:	C 84.4, 84.6; H 9.8, 9.95
$C_{20}H_{28}O$.	Calculated %:	C 84.5; H 9.9

Analysis of the Ketone XXV B

	Found %:	C 84.4, 84.5; H 9.8, 9.9
$C_{20}H_{28}O$.	Calculated %:	C 84.5; H 9.9

Attempts to form derivatives by reaction at the carbonyl group were not successful.

Hydrogenation of the Ketone XXV A. The ketone XXV A of m.p. 143-144° (150 mg) was hydrogenated in 10 ml of alcohol in presence of an Adams platinum catalyst (10 mg). Hydrogenation was complete in five minutes, when 14.1 ml (22°, 760 mm) of hydrogen had been absorbed (theory requires 14.7 ml, hydrogen consumed in the reduction of the platinum oxide being taken into account). The usual treatment and crystallization from petroleum ether yielded 70 mg of the ketone XXVI A, m.p. 122-123°.

	Found %:	C 83.6; H 10.5
$C_{20}H_{30}O$.	Calculated %:	C 83.9; H 10.5

In admixture with the ketone prepared in our laboratory by another method [2] there was no depression in melting point.

An attempt to bring about the isomerization of the ketone XXVI A in boiling hydrochloric and acetic acids gave a negative result, the ketone being recovered unchanged. Moreover, the ketone was not hydrogenated when treated in presence of a platinum catalyst in acetic acid.

Hydrogenation of the Ketone XXV B. The ketone XXV B, m.p. 122-123° (150 mg), was hydrogenated in alcohol in the manner described above, the product being 60 mg of the ketone XXVI B, m.p. 127-128°.

	Found %:	C 83.8, 83.9; H 10.5, 10.7
$C_{20}H_{30}O$.	Calculated %:	C 83.9; H 10.5

In admixture with the original ketone it melted at 104-117°. The ketone XXVI B could not be hydrogenated in acetic acid in presence of platinum and did not undergo isomerization in boiling hydrochloric and acetic acids.

Attempt to Oxidize the Ketone XXV B with Iodine and Alkali. Solutions of 2.65 g of iodine in 25 ml of methanol and of 5 g of caustic potash in a mixture of 10 ml of water and 15 ml of methanol were added with stirring to a solution of 1 g of the ketone XXV B, m.p. 122-123°, in 25 ml of methanol. The addition was carried out at 20° over a period of 50 minutes, care being taken that there was always excess of iodine. When half of the solutions had been added, a precipitate began to form, and this gradually increased in amount. The mixture was stirred for five hours, and the precipitate was then filtered off and washed with methanol (350 mg of fine crystals). Crystallization from methanol yielded 220 mg of a diiodo compound, m.p. 128-129° (softening, however, at 117°).

	Found %:	C 44.7, 44.6; H 5.5, 5.3; I 47.2, 47.5
$C_{20}H_{30}OI_2$.	Calculated %:	C 44.4; H 5.6; I 47.0

Kizhner Reduction of the Ketone XXV B. The ketone XXV B of m.p. 122-123° (1.7 g) was mixed with 5 ml of diethylene glycol, 7 ml of dioxane, and 1.2 ml of hydrazine hydrate, and heated for five minutes in a water bath. The mixture was transferred to a Favorsky flask having ground joints, and a solution of 1.4 g of sodium in 28 ml of diethylene glycol was added. The turbid mixture was heated in a feeble current of nitrogen at 205-210° for 15 hours, when the dioxane and a small amount of water were driven off.

The reaction mixture was diluted with twice its volume of water and extracted with ether; the ether extracts were washed twice with 10% hydrochloric acid and with water. The ether was driven off, and the residue was vacuum-distilled, yielding 1.3 g (81%) of the hydrocarbon XXVII as a thick colorless, almost odorless liquid, b.p. 145-147° (2 mm) and n_D^{20} 1.5330.

	Found %:	C 88.2; H 11.1
$C_{20}H_{30}$.	Calculated %:	C 88.9; H 11.1

Dehydrogenation of the Hydrocarbon XXVII. A mixture of 1.1 g of the hydrocarbon XXVII, 1.2 g of palladized charcoal (10% Pd), and 18 ml of benzene was heated in a rotating autoclave in an atmosphere of nitrogen (initial pressure, 30 atm) at 350° for six hours. After filtration and removal of benzene, the residue (0.9 g) was dissolved in 7 ml of petroleum ether and set aside at −70° for two days. Crystals (26 mg), m.p. about 90°, separated. The mother liquor was chromatographed through 10 g of aluminum oxide, and a further 30 mg of crystalline product was isolated as a result. The crops of crystals were united and crystallized twice from petroleum ether, yielding 20 mg of hydrocarbon XXVIII, m.p. 119-121°. In admixture with Diels' hydrocarbon, prepared previously by another method [2], it showed no depression in melting point.

Its compound with trinitrobenzene melted at 146-147°, and again it gave no depression in admixture with an authentic sample.

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-Methyl-2-cyclohexen-1-one (X). A mixture of 10 g of V with 90 g of 2-methyl-2-cyclohexen-1-one (X) was heated for ten hours at 170°

in a glass tube in an atmosphere of carbon dioxide. The excess (84 g) of ketone was distilled off at 15 mm, and unchanged hydrocarbon (3 g) was distilled off at 1 mm. The residual viscous liquid (10 g) was mixed with 10 ml of alcohol, and crystallization quickly set in. Altogether (including material obtained from the mother liquors) 4.7 g of a crystalline mixture of steroid ketones was obtained (43% yield, based on the triene V that had reacted). Fractional crystallization from methanol yielded:

1. Ketone XXX A, m.p. 130-130.5°, 2.0 g.

	Found %:	C 84.3, 84.3; H 9.9, 9.9
$C_{20}H_{28}O$.	Calculated %:	C 84.5; H 9.9

After being washed with benzene, the semicarbazone melted at 245-247° (in a sealed capillary).

	Found %:	N 12.5, 12.6
$C_{21}H_{31}ON_3$.	Calculated %:	N 12.3

2. Ketone XXX B, m.p. 118-119°, 0.6 g.

	Found %:	C 84.5, 84.4; H 9.6, 10.0
$C_{20}H_{28}O$.	Calculated %:	C 84.5; H 9.9

3. Ketone XXX C, m.p. 133-133.5°, 0.4 g.

	Found %:	C 84.4, 84.6; H 9.9, 9.9
$C_{20}H_{28}O$.	Calculated %:	C 84.5; H 9.9

A mixture of ketone XXX C with ketone XXX A melted at 102-107°.

Hydrogenation of the Ketones XXX A, XXX B, and XXX C. The ketone XXX A of m.p. 130-130.5° (100 mg) was hydrogenated in 10 ml of alcohol in presence of an Adams platinum catalyst (the amount of hydrogen used was not measured). The usual treatment, followed by crystallizations from alcohol and from petroleum ether, yielded 40 mg of the ketone XXXI A, m.p. 119-120°.

	Found %:	C 84.0, 83.7; H 10.4, 10.55
$C_{20}H_{30}O$.	Calculated %:	C 83.9; H 10.5

In a similar way, 150 mg of ketone XXX B, m.p. 118-119°, yielded 50 mg of the ketone XXXI B, m.p. 114-115° (after two crystallizations from methanol).

	Found %:	C 84.0, 83.9; H 10.7, 10.7
$C_{20}H_{30}O$.	Calculated %:	C 83.9; H 10.5

In admixture with the original ketone (XXX B) it melted at 101-107°.

From 150 mg of the ketone XXX C, m.p. 133-133.5°, 40 mg of the ketone XXXI C, m.p. 132-133° (from methanol), was obtained.

	Found %:	C 83.7, 83.8; H 10.6, 10.7
$C_{20}H_{30}O$.	Calculated %:	C 83.9; H 10.5

In admixture with the original ketone (XXX C), a considerable depression in melting point was obtained.

Isomerization of the Ketone XXXI A. a) A mixture of 200 mg of the ketone XXXI A, m.p. 119-120°, 5 ml of acetic acid, 5 ml of hydrochloric acid, and 7 ml of toluene was boiled under reflux for seven hours. The toluene layer was separated, neutralized by agitation with a 5% solution of caustic soda, and filtered. The solvent was driven off under reduced pressure, and the residue was crystallized from petroleum ether, yielding 150 mg of the ketone XXXI D, m.p. 137-138°. This ketone showed no depression when mixed with the ketone obtained at the same time in our laboratory by another method [4] (see the ketone VII in Communication 155).

b) The ketone XXXI A of m.p. 119-120° (100 mg) was shaken in 5 ml of acetic acid in an atmosphere of hydrogen in presence of an Adams platinum catalyst for two hours. The usual treatment and crystallization from petroleum ether yielded 80 mg of the ketone XXXI D, m.p. 137-138°; in admixture with the ketone prepared as above (a), it showed no depression in melting point.

Isomerization of the Ketone XXXI B. This was carried out by the action of hydrochloric acid, as described above, 100 mg of the ketone XXXI B, m.p. 114-115°, yielding 60 mg of the ketone XXXI C, m.p. 121-121.5° (from alcohol). The ketone XXXI C was not affected by the action of hydrochloric acid.

Action of Methylmagnesium Bromide on the Ketone XXX A. A solution of 1.2 g of the ketone XXX A, m.p. 130°, in a mixture of 25 ml of ether and 10 ml of benzene was added with stirring to a Grignard reagent prepared from 0.5 g of magnesium, 3.1 g of methyl bromide, and 25 ml of absolute ether. The ether was driven off and replaced by 20 ml of benzene, and the mixture was heated at 80° for two hours. The mixture, on cooling, was decomposed with ice followed by hydrochloric acid. The benzene layer was dried, and the solvent was distilled off. The residue crystallized out and was recrystallized from methanol, yielding 0.9 g of the tetracyclic alcohol XXX D, m.p. 158-159°.

	Found %:	C 83.9, 84.1; H 10.9, 10.8
$C_{21}H_{32}O$.	Calculated %:	C 84.0; H 10.7

The tertiary alcohol obtained (XXX D) was dehydrated with potassium hydrogen sulfate in xylene at 150°. The product, without purification, was dehydrogenated in presence of palladized charcoal at 340-350°. Chromatography of the product yielded 8 mg of chrysene, m.p. 243-245°. Its compound with trinitrobenzene melted at 186.5-187°.

The following data regarding chrysene, 1-methylchrysene and 4-methylchrysene are given in the literature:

Substance	Reference	M.p. (°C)	M. p. (°C) of trinitrobenzene compound
Chrysene	[17]	250-251	186-188
1-Methylchrysene	[18]	254-255	174-176
4-Methylchrysene	[19]	151	–

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-Cyclohexen-1-one (IX). A mixture of 2.1 g of the triene V and 13 g of 2-cyclohexen-1-one (IX) was heated for ten hours at 170° in a glass tube in an atmosphere of carbon dioxide. Fractionation of the reaction mixture yielded 12 g of unchanged cyclohexenone, 0.9 g of the triene V, and 1.7 g of a mixture of the isomeric steroid ketones XXXII in the form of a slightly yellowish viscous liquid, b.p. 137-139° at 0.06 mm; n_D^{20} 1.5420. Neither by standing nor by dissolution in alcohol and cooling could the liquid be caused to crystallize.

	Found %:	C 83.9, 84.0; H 9.8, 9.85
$C_{19}H_{26}O$.	Calculated %:	C 84.4; H 9.6

After recrystallization from methanol the semicarbazone melted at 237-237.5° (in a sealed capillary).

	Found %:	N 13.15; 13.05
$C_{20}H_{29}ON_3$.	Calculated %:	N 12.84

Condensation of 3,4,4a,5,8,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with p-Benzoquinone (XI). A mixture of 0.9 g of the triene V and 0.7 g of sublimed p-benzoquinone was dissolved in 15 ml of absolute dioxane and heated in a glass tube in an atmosphere of carbon dioxide for three hours at 65°. The dioxane was distilled off under reduced pressure, and the residue crystallized out, yielding 0.5 g (about 30%) of slightly yellowish crystals of the diketone XXXIII, m.p. 92-105°. After two crystallizations from methanol, well formed crystals were obtained that melted at 108-118° (in a sealed capillary). The melting point did not alter after the first and second recrystallizations; some change evidently took place in the substance when it was melted*.

	Found %:	C 80.8, 80.9; H 7.9, 7.9
$C_{19}H_{22}O_2$.	Calculated %:	C 80.85; H 7.8

It was not found possible to obtain either a semicarbazone or a dinitrophenylhydrazone.

Condensation of 3,4,4a,5,8a-Hexahydro-8a-methyl-1-vinylnaphthalene (V) with 3,5-Dimethyl-3-cyclopentene-1,2-dione (XII). A mixture of 0.9 g of the triene V, 0.7 g of the dione XII, and 5 ml of dioxane was heated for six hours in a boiling water bath in a glass tube in an atmosphere of carbon dioxide. The dioxane was distilled off, and the residue crystallized out, yielding 0.5 g (about 30%) of the diketone XXXIV, m.p. 92-110°. Two crystallizations from alcohol yielded well-formed yellow crystals of m.p. 100-110°.

	Found %:	C 80.2, 80.2; H 8.8, 8.8
$C_{20}H_{26}O_2$.	Calculated %:	C 80.5; H 8.7

*Butz and Gaddis [12] give an m.p. of 166-170° for this product.

The extended melting range is no doubt to be explained by the ready isomerization of the diketone XXXIV into the hydroxy ketone XXXV. We have observed such isomerizations in our laboratory in other cases [6].

The isomerization of the diketone XXXIV into the hydroxy ketone XXXV was effected by addition of a drop of piperidine to a solution of 50 mg of the diketone XXXIV in 2 ml of dioxane. After ten minutes the solution was diluted with an equal amount of water, when colorless crystals of the hydroxy ketone XXXV, m.p. 131-132°, separated. They gave a violet coloration with ferric chloride, whereas the original diketone (XXXIV) did not give this reaction.

SUMMARY

1. The complete syntheses of a number of new steroid ketones have been effected by condensation of 3,4,4a, 5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V) with 2-methyl-2-cyclopenten-1-one (VII), 2,4-dimethyl-2-cyclopentene-1-one (VIII), 2-cyclohexen-1-one (IX), 2-methyl-2-cyclohexen-1-one (X), p-benzoquinone (XI), and 3,5-dimethyl-3-cyclopentene-1,2-dione (XII). The steroid ketones obtained by the condensation of the triene V with the cyclopentenones VII and VIII have the so-called "inverted structure, and the main product of the condensation of the triene V with citraconic anhydride has the same structure.

2. It has been shown that displacement of the double bond in the 9(11) position readily occurs when steroid ketones are heated with hydrochloric acid or are shaken in acetic acid solution in presence of a platinum catalyst.

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SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XXIII. SYNTHESIS OF SULFUR ANALOGS OF STEROIDS BY DIENE CONDENSATION OF CYCLIC γ-KETO SULFONES WITH BICYCLIC DIENES

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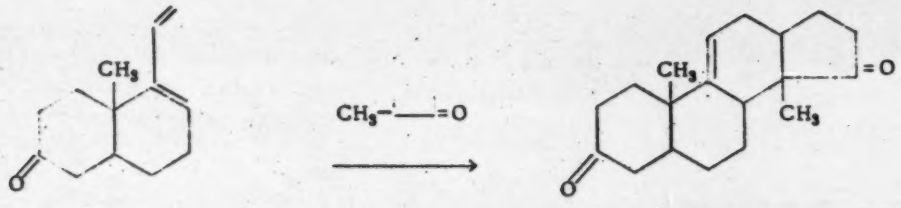
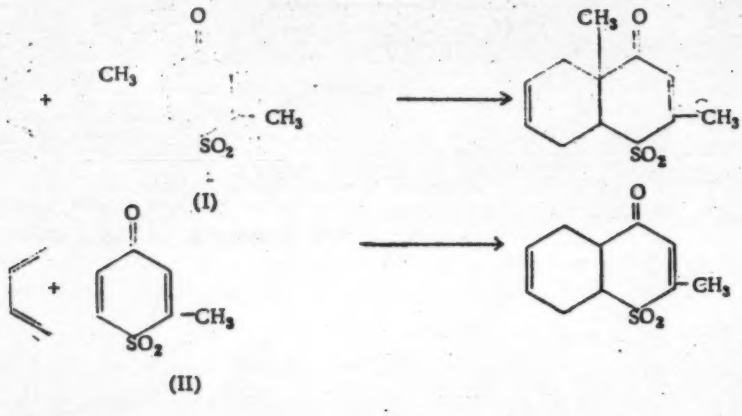
For some years we have been studying in detail the diene condensations of various bicyclic dienes with α,β-unsaturated cyclic ketones with the object of synthesizing polycyclic compounds related to steroids. These syntheses may be illustrated by the example of the diene condensation of 2-methyl-2-penten-1-one with 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone:



As will be seen from this equation, this method can readily yield various steroid ketones having the so-called "inverted" D ring [1]. As a development of these investigations we decided to study the condensation of bicyclic dienes also with unsaturated cyclic γ-keto sulfones, and so effect the synthesis of sulfur analogs of steroid compounds.

In one of our previous papers we have described the condensation of 1,1-dioxides of 4H-1-thiapyran-4-ones and of dihydro-4H-1-thiapyran-4-ones with 1,3-butadiene [2]. It was then found that the dioxides of substituted 4H-1-thiapyran-4-ones undergo this condensation with greater difficulty than the dioxide of 4H-1-thiapyran-4-one itself. It was established also that the ability of dioxides of substituted 4H-1-thiapyran-4-ones to take part in the diene synthesis depends on the position of the substituent in the nucleus. The introduction of methyl α to the carbonyl makes the diene synthesis appreciably more difficult, but its introduction β to the carbonyl makes the condensation impossible at temperatures of up to 200°. Thus, the 1,1-dioxides of 2,5-dimethyl- and 2-methyl-4H-1-thiapyran-4-ones (I and II) condense with only one molecule of 1,3-butadiene at 200°, good yields of 1,1-dioxides of cis-4a,5,8,8a-tetrahydrothiachromones being obtained:

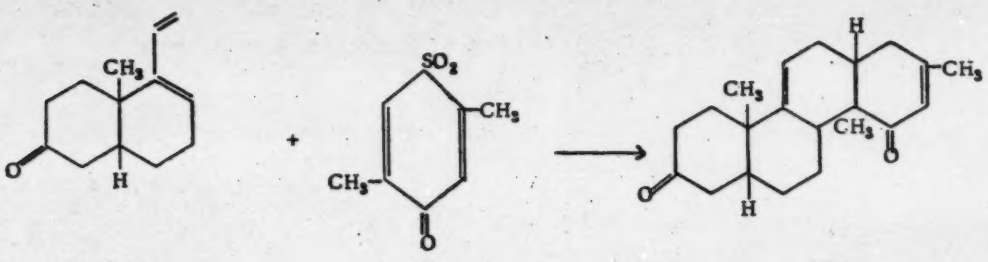


(I)

(II)

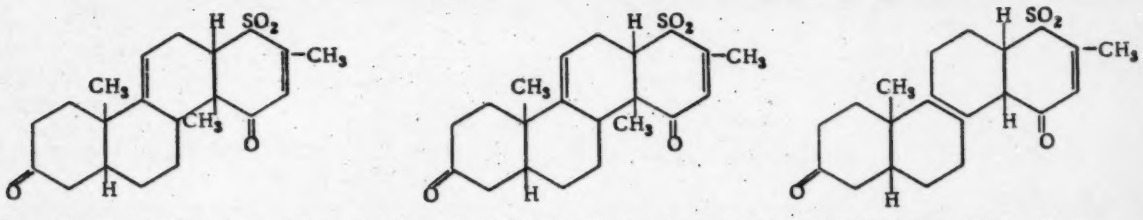
In this paper we describe the condensation of the unsaturated cyclic γ-keto sulfones I and II with various bicyclic ketones; the products have the skeletons of phenanthro[2,1-bc]thiapyran and flureno[2,1-bc]thiapyran and are sulfur analogs of homosteroids and related compounds. In the condensation of the keto sulfone I with various

bicyclic dienes, the components were taken in equimolecular proportions and the reaction was carried out in dioxane solution at 170°; tetracyclic keto sulfones were obtained in 30-70% yield. Thus, heating of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)naphthalenone (III) with the sulfone I in dioxane solution at 170° for 13 hours yielded a mixture of two isomeric tetracyclic diketo sulfones (IV) with an overall yield of 71%:

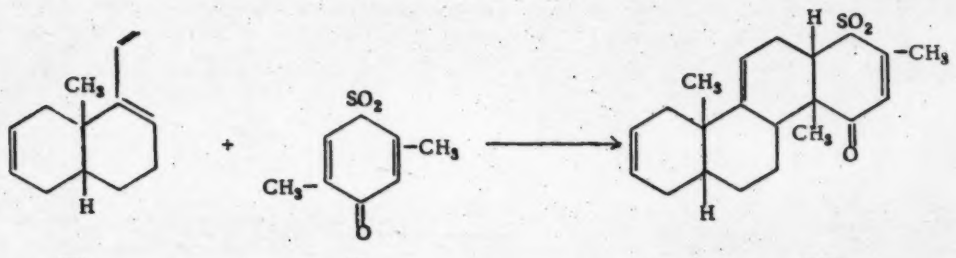


(III) (I) (IV)

It is probable that here, as in the case of α,β-unsaturated cyclic ketones [1], "inverted" structures are formed, the isomerism of the tetracyclic sulfones obtained being explained by differences in the configurations of substituents at (C-13)-(C-14), by difference in configuration at C-8, or by difference in the position of one of the double bonds, as can be seen from the following formulas:

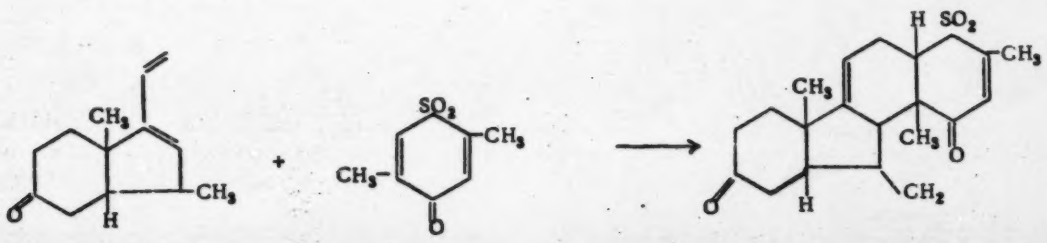


By condensation of the keto sulfone I with 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V) in dioxane solution at 170° for six hours, a mixture of isomeric tetracyclic keto sulfones (VI) was obtained with an overall yield of 60%:



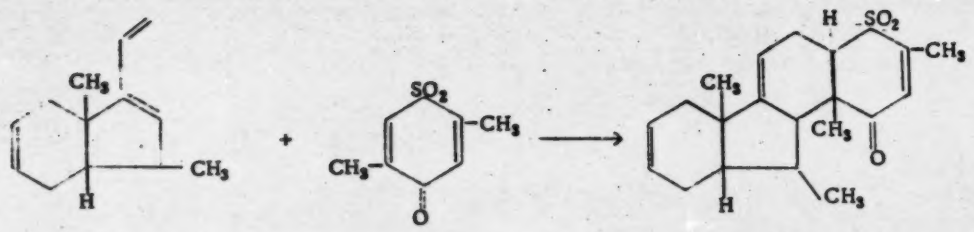
(V) (I) (VI)

When the keto sulfone I was condensed with bicyclic dienes of the indene series, the yield of condensation products was considerably lower. Thus, heating of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (VII) with the keto sulfone I in dioxane solution at 170° for six hours yielded a mixture of isomeric tetracyclic keto sulfones (VIII) with an overall yield of 31.5%:



(VII) (I) (VIII)

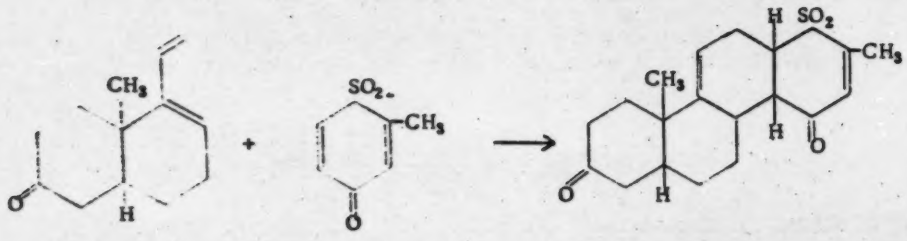
Heating of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinylindene (IX) with the sulfone I in dioxane solution at 170° for nine hours yielded a mixture of isomeric tetracyclic keto sulfones (X) with an overall yield of 37%:



(IX) (I) (X)

In all the condensations described, therefore, two isomeric crystalline products were obtained.

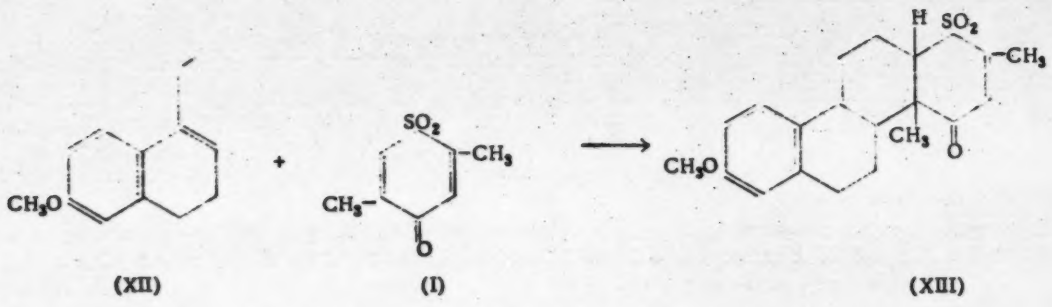
When the diene III was condensed with the keto sulfone II in dioxane solution at 145° for six hours, only one tetracyclic diketo sulfone (XI) was isolated, the yield being 60%:



(III) (II) (XI)

In all of the tetracyclic keto sulfones that we have prepared the A-B and C-D rings are united in the cis-position, since all of these compounds were built up entirely by the diene-condensation method.

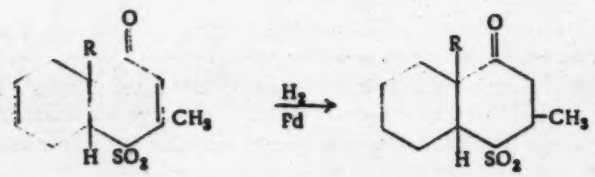
We prepared also the sulfur analog of homoestrone by condensing 3,4-dihydro-6-methoxy-1-vinylnaphthalene (XII) with the keto sulfone I in dioxane solution at 170° for six hours. In this case also we isolated only one tetracyclic keto sulfone (XIII), the yield being 37%:



(XII) (I) (XIII)

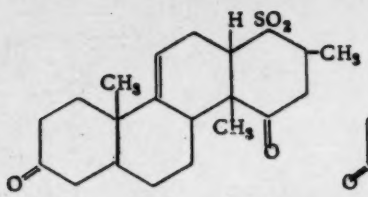
In the methoxy keto sulfone XIII, the C and D rings are united in the cis-position.

As we have shown previously, the products of the diene condensation of 1,3-butadiene with dioxides of substituted 4H-1-thiapyran-4-ones readily take up four atoms of hydrogen in presence of a palladium catalyst [3, 4]:

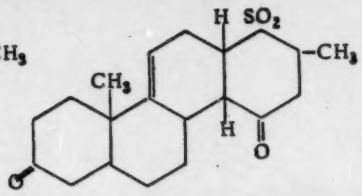


R = H; CH_3

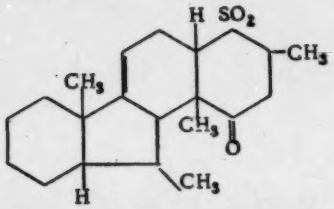
It was found that, when the above-described tetracyclic condensation products were reduced in presence of a palladium catalyst, only the double bonds in rings A and D were hydrogenated, the double bond in ring C formed in the diene condensation being unaffected. Thus, when the isomeric diketo sulfones IV were hydrogenated in presence of a palladium catalyst, only one molecule of hydrogen was absorbed, with formation of the isomeric diketo sulfones XIV. Hydrogenation of the diketo sulfone XI under like conditions yielded the compound XV:



(XIV)



(XV)

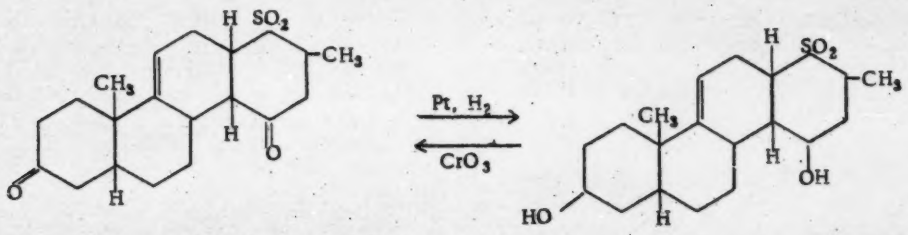


(XVI)

Even when the hydrogenation of the diketo sulfone XI was performed under more severe conditions in presence of palladized charcoal at elevated temperature and pressure, the same product (IV) was obtained.

In the hydrogenation of the low-melting isomer of X, only two molecules of hydrogen were absorbed, and the product of partial hydrogenation, XVI, was formed also. The compounds XIV, XV, and XVI do not decolorize permanganate solution.

When the diketo sulfone XV was hydrogenated in acetic acid solution in presence of platinum oxide and chloroplatinic acid, both carbonyls were reduced, and the unsaturated diol (XVII) and its diacetic ester were obtained. In this case also, the double bond in the ring C was preserved. The structure of the unsaturated diol (XVII) was proved by oxidizing it back into the original diketo sulfone XV:



(XV) (XVII)

The diacetic ester of the diol XVII was prepared also by acetylating the diol with acetyl chloride in glacial acetic acid solution. The difficulties experienced in the hydrogenation of the C ring formed as a result of the condensation of an unsaturated cyclic γ-keto sulfone with a bicyclic diene, and also data available concerning the shift of such a bond in carbocyclic compounds under the conditions of the diene synthesis [1], give us reason to suggest the possibility of the shift of the double bond in the tetracyclic sulfones described from the 9(11)- to the 8(9)-position. The diketo sulfones XI and XV, like unsaturated bicyclic ketones [3, 4, 5], do not isomerize in presence of sodium methoxide into the corresponding compounds of the trans series.

EXPERIMENTAL

The Tetracyclic Diketo Sulfone IV. A mixture of 4.8 g of 3,4,4a,7,8,8a-hexahydro-4a-methyl-5-vinyl-2(1H)-naphthalenone (III) [b.p. 136-138° (7 mm); n_D^{20} 1.5250] [6], 4.3 g of 2,5-dimethyl-4H-1-thiapyran-4-one 1,1-dioxide (I) (m.p. 138-139°) [2], and 15 ml of dioxane was heated in presence of 0.05 g of pyrogallol in a sealed glass tube in an atmosphere of nitrogen for six hours at 170°. After being interrupted overnight, heating was continued for a further seven hours. After removal of solvent under reduced pressure, ether was added, and 6.5 g of crystals of the tetracyclic diketo sulfone IV was isolated. Some resin and a small amount of the original diene remained in the

residue. By fractional crystallization from methanol, followed by passage of benzene solutions of the separate fractions through a layer of anhydrous aluminum oxide, it was found possible to isolate 3 g of the low-melting isomer of IV, m.p. 212-213° (in a sealed capillary). The substance crystallized in the form of fine plates.

Found %: C 66.11; 66.21; H 7.29; 7.45; S 8.50
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

In addition, 0.6 g of crystals, m.p. 225-226° (in a sealed capillary), was isolated. This substance crystallized in the form of rosettes; it was the high-melting isomer of IV.

Found %: C 66.54; 66.26; H 7.10; 7.19; S 8.77
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

A mixture of the two isomers melted at 208-218° (softening began at 190°).

The Tetracyclic Keto Sulfone VI. A mixture of 1 g of 3,4,4a,5,8,8a-hexahydro-8a-methyl-1-vinylnaphthalene (V) [b.p. 82-84° (2 mm); n_D^{20} 1.5240] [7], 0.99 g of 2,5-dimethyl-4H-1-thiapyran-4-one 1,1-dioxide (I), and 10 ml of dioxane was heated in presence of 0.02 g of pyrogallol in a steel tube for six hours at 170-175°. The solvent was distilled off under reduced pressure, and the residue, after being treated with ether, yielded 1.2 g of crystals, which were separated by fractional crystallization from alcohol into two fractions.

Repeated crystallization of Fraction I (m.p. 192-195°) from alcohol yielded fine silvery crystals of the high-melting isomer of the tetracyclic keto sulfone VI, m.p. 208-209.5°.

Found %: C 69.35; 69.51; H 7.60; 7.65; S 9.12; 9.30
$C_{20}H_{26}O_3S$. Calculated %: C 69.33; H 7.56 S 9.25

From Fraction II, m.p. 165-178°, crystals of the low-melting isomer of VI were obtained in the form of large oblong prisms, m.p. 182-183°.

Found %: C 69.42; 69.32; H 7.56; 7.59; S 9.62; 9.15
$C_{20}H_{26}O_3S$. Calculated %: C 69.33 H 7.56 S 9.25

The Tetracyclic Diketo Sulfone VIII. A mixture of 0.75 g of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (VII) (b.p. 108-109°; n_D^{22} 1.5070) [8], 0.75 g of the keto sulfone I, and 8 ml of dioxane was heated in presence of 0.01 g of pyrogallol in a steel tube for six hours at 170-175°. The solvent was distilled off under reduced pressure, and the resin that remained was treated with ether; two fractions of crystals were obtained. From Fraction I (0.25 g, m.p. about 220°) recrystallizations from alcohol and acetone yielded plates of the high-melting isomer of the tetracyclic diketo sulfone VIII, m.p. 235-236°.

Found %: C 66.23; H 7.24; S 8.78
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

The mother liquor yielded 40 mg of the original sulfone.

From Fraction II (0.2 g, m.p. 160-164°) fractional crystallization from alcohol yielded needles of the low-melting isomer of VIII, m.p. 170-171°.

Found %: C 65.95; 66.02; H 7.19; 7.15; S 8.60; 8.68
$C_{20}H_{26}O_4S$. Calculated %: C 66.26; H 7.23; S 8.84

The Tetracyclic Keto Sulfone X. A mixture of 2 g of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinylindene (IX) [b.p. 67-68° (3 mm); n_D^{20} 1.5065] [9], 1.8 g of the keto sulfone I, and 10 ml of dioxane was heated in a glass tube for 4 hours 30 minutes at 170°. Heating, after interruption overnight, was continued for a further 4 hours 30 minutes at 167-170°. The solvent was distilled off under reduced pressure, and ether was added to the residue; 1.4 g of crystals was isolated. Three recrystallizations from alcohol yielded the low-melting isomer of the tetracyclic keto sulfone X in the form of needles, m.p. 158-159° (in a sealed capillary; in an open capillary the substance melted 10° lower).

Found %: C 69.03; H 7.91; S 9.16
$C_{20}H_{26}O_3S$. Calculated %: C 69.33; H 7.56; S 9.25

In addition, prisms of the high-melting isomer of X, m.p. 172-173° (in a sealed capillary), were isolated.

Found %: C 69.42; H 7.67; S 9.09
$C_{20}H_{26}O_3S$. Calculated %: C 69.33; H 7.56; S 9.25

The Tetracyclic Diketo Sulfone XI. A mixture of 1.5 g of the diene III [b.p. 125-127° (4 mm); n_D^{25} 1.5250], 1.2 g of 2-methyl-4H-1-thiapyran-4-one 1,1-dioxide (II) (m.p. 141°), and 7 ml of dioxane was heated in presence of 0.03 g of pyrogallol in a glass tube in an atmosphere of nitrogen for six hours at 143-145°. The solvent was distilled off under reduced pressure, and methanol was added to the residue; 2 g of crystals, m.p. about 200°, was isolated. The residue consisted of resin and a small amount of the starting materials. Fractional crystallization from methanol, followed by passage of benzene solutions of the separate fractions through a column of anhydrous aluminum oxide, yielded 1.7 g of the tetracyclic diketo sulfone XI, m.p. 215-215.5° (in a sealed capillary).

	Found %:	C 65.49; 65.71;	H 7.12; 7.00;	S 9.31; 9.37
$C_{19}H_{24}O_4S$.	Calculated %:	C 65.49;	H 6.94	S 9.20

After being boiled in methanol solution containing 0.1% of sodium for 15 minutes, the sulfone XI was recovered unchanged. Boiling for two hours caused resinification.

The Tetracyclic Methoxy Keto Sulfone XIII. A mixture of 1.2 g of 3,4-dihydro-6-methoxy-1-vinylnaphthalene (XII) [b.p. 125-132° (0.05 mm); n_D^{19} 1.5805] [10], 1 g of the keto sulfone I (m.p. 138-139°), and 10 ml of dioxane was heated in presence of pyrogallol in a steel tube for six hours at 170-175°. The solution was poured off, and at the bottom of the tube there remained 0.6 g of crystals of the tetracyclic methoxy keto sulfone XIII. The solvent was driven off, yielding a mixture of crystals, from which a further 200 mg of the methoxy keto sulfone XIII was isolated, together with 200 mg of the original sulfone (I) (m.p. 137-138°). A mixed melting point test of the latter and some of the original sulfone gave no depression. The pure tetracyclic methoxy keto sulfone XIII, obtained by recrystallization from benzene, melted at 221-221.5°.

	Found %:	C 67.12; 67.25;	H 6.23; 6.32;	S 8.98; 8.86
$C_{21}H_{22}O_4S$.	Calculated %:	C 67.02;	H 6.19	S 8.94

The Tetracyclic Diketo Sulfone XIV. a) A solution of 0.7 g of the low melting isomer of the diketo sulfone IV, m.p. 212-213°, in dioxane was hydrogenated in presence of palladium on a calcium carbonate carrier. The amount of hydrogen absorbed in one hour was 55 ml at 18° and 743 mm (one molecule); hydrogenation was then discontinued. After removal of solvent, two crystallizations from alcohol yielded the diketo sulfone XIV, m.p. 240-241° (in a sealed capillary).

	Found %:	C 66.04; 65.86;	H 7.67; 7.84;	S 8.74; 8.76
$C_{20}H_{22}O_4S$.	Calculated %:	C 65.91;	H 7.75;	S 8.80

The compound XIV did not decolorize permanganate solution. An attempt was made to hydrogenate the substance IV completely in presence of a palladium catalyst at 100° and also in presence of platinum oxide in a dioxane medium, but in both cases only XIV, m.p. 240-241°, was obtained.

b) A solution of 0.2 g of the high-melting isomer of the diketo sulfone IV, m.p. 224-225°, in a mixture of methanol and benzene was hydrogenated in presence of a palladium catalyst. In the course of 30 minutes about 15 ml (one molecule) of hydrogen was absorbed, and the hydrogenation was discontinued. Two crystallizations from alcohol yielded the second isomer of the diketo sulfone XIV, m.p. 231-232° (in a sealed capillary).

	Found %:	C 65.91; 65.65;	H 7.94; 7.87;	S 8.95
$C_{20}H_{22}O_4S$.	Calculated %:	C 65.91;	H 7.75;	S 8.80

A mixture with the isomeric sulfone (XIV) (m.p. 240-241°) melted at 205-210°.

The Tetracyclic Diketo Sulfone XV. a) An acetone solution of 0.24 g of the diketo sulfone XI, m.p. 214-215°, was hydrogenated in presence of a palladium catalyst. In the course of 30 minutes about 20 ml (one molecule) of hydrogen at 22° and 753.8 mm had been absorbed; hydrogenation was then discontinued. After removal of acetone and two crystallizations of the residue from methanol, the diketo sulfone XV of m.p. 216-216.5° (in a sealed capillary) was obtained.

	Found %:	C 64.68; 64.86;	H 7.53; 7.53	
$C_{19}H_{26}O_4S$.	Calculated %:	C 65.11;	H 7.48	

The product (XV) did not decolorize a permanganate solution. A mixture with the original diketo sulfone (XI) melted at 199-200°, with preliminary sintering at 197°. Boiling of the sulfone XV in methanol containing 0.1% of sodium for 30 minutes was without effect, the substance being recovered unchanged. Boiling for two hours caused resinification.

b) The diketo sulfone XI of m.p. 214-215° (0.675 g) was hydrogenated in 25 ml of dioxane in presence of 0.5 g of palladized charcoal (10% Pd) in an autoclave at 60 atm and 100-120° for four hours. The solvent was distilled off,

and alcohol was added; 0.32 g of a substance was isolated, and this, after recrystallization from alcohol, melted at 209-210°. After passage of a benzene solution of the substance through a column of aluminum oxide, the melting point rose to 215-215.5°. In admixture with the above-described partial-hydrogenation product (XV), no depression of melting point was observed.

The Tetracyclic Keto Sulfone XVI. The diene-condensation product X of m.p. 158-159° (0.3 g) was hydrogenated in dioxane solution in presence of a palladium catalyst until no further hydrogen was absorbed. Recrystallization from alcohol yielded the keto sulfone XVI, m.p. 159-160° (in a sealed capillary).

	Found %:	C 68.68; 68.43;	H 8.68. 8.67;	S 9.19; 9.35
$C_{28}H_{30}O_3S$.	Calculated %:	C 68.49;	H 8.63	S 9.15

A mixture of this with the original material melted at 134-142°.

The Tetracyclic Diol XVII. The diketo sulfone XV of m.p. 215-216° (0.28 g) was hydrogenated in 10 ml of glacial acetic acid in presence of platinum oxide and chloroplatinic acid; about 45 ml of hydrogen was absorbed. The acetic acid was distilled off, and benzene was added to the residue; 100 mg of crystals was separated. The benzene solution was passed through an aluminum oxide column; a further 20 mg of crystals together with some clear colorless resin was obtained. Three recrystallizations from benzene yielded the diol XVII, m.p. 245-246° (in a sealed capillary).

	Found %:	C 67.23; 67.02;	H 8.47; 8.51;	S 8.00; 7.95
$C_{28}H_{36}O_4S \cdot {}^1/_2C_6H_6$	Calculated %:	C 67.13;	H 8.26	S 7.96

The diol XVII is readily soluble in alcohol. The colorless glassy resin corresponded in analysis to the diacetic ester of the diol.

	Found %:	C 62.93; 63.14;	H 8.39; 8.24;	S 6.90; 6.68
$C_{32}H_{36}O_6S$.	Calculated %:	C 62.99;	H 7.81;	S 7.31

Oxidation of the Diol XVII. The diol XVII of m.p. 242-244° (0.065 g) was oxidized with chromic anhydride in glacial acetic acid solution; 0.029 g of chromic anhydride was consumed in the oxidation (about 2 atoms of oxygen per molecule of diol). The acetic acid was distilled off under reduced pressure, and the residue was extracted with benzene, the extract being then passed through an aluminum oxide column. Benzene was distilled off, and a crystalline substance was isolated, which melted, after recrystallization from alcohol, at 214-215°. In admixture with the diketo sulfone XV it showed no depression in melting point.

Acetylation of the Diol XVII. A mixture of 0.1 g of the diol of m.p. 243-244°, 1.5 ml of acetyl chloride, and 1 ml of glacial acetic acid was heated in an oil bath at 110° for 90 minutes (until hydrogen chloride was no longer evolved). The solvent was distilled off under reduced pressure, leaving a residue of clear colorless resin, which was passed, in dioxane solution, through an aluminum oxide column, and then dried for a long time in a vacuum desiccator. It corresponded in analysis to the diacetic ester of the diol XVII.

	Found %:	C 61.84; 61.94;	H 7.84; 7.84;	S 7.41; 7.32
$C_{32}H_{36}O_6S$.	Calculated %:	C 62.99;	H 7.81;	S 7.31

SUMMARY

1. The tetracyclic keto sulfones IV, VI, and XIII, having the phenanthro[2,1-bc]thiapyran ring system, have been prepared in yields of 70, 61, and 37% respectively by the condensation of the γ-keto sulfone I with the bicyclic dienes III, V, and XII.

2. The tetracyclic keto sulfones VIII and X, having the fluoreno[2,1-bc]thiapyran ring system, have been prepared in yields of 31 and 37% respectively by the condensation of the γ-keto sulfone I with the bicyclic dienes VII and IX.

3. The tetracyclic steroid keto sulfone XI has been prepared in 60% yield by condensation of the cyclic γ-keto sulfone II with the bicyclic diene III.

4. When the tetracyclic keto sulfones IV, X, and XI were hydrogenated in presence of Pd and Pt catalysts, the double bond formed as a result of the diene synthesis was not affected.

5. Hydrogenation of the unsaturated diketo sulfone XV in presence of a Pt catalyst yielded the unsaturated diol XVII.

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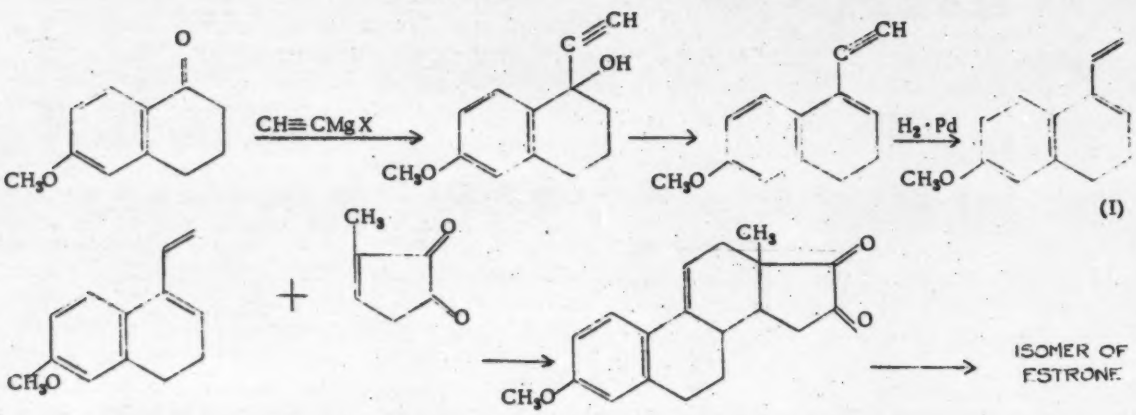
SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS

COMMUNICATION XXV. SYNTHESIS OF COMPOUNDS RELATED TO ESTRONE BY THE DIENE-CONDENSATION METHOD

I. N. Nazarov and I. L. Kotlyarevsky

In previous communications from our laboratory [1] we have described a simple method for the synthesis of tetracyclic steroid ketones by the diene condensation of α,β-unsaturated cyclic ketones with bicyclic dienes, such as 1,2,3,4,4a,5,6,8a-octahydro-8-vinylnaphthalene. We have thus prepared a group of steroid compounds related to the male hormones. In continuation of our investigations in this field, we decided to make use of this method for the synthesis of polycyclic ketones related to estrone.

A previous attempt to synthesize compounds of the estrone series has been made by Dane and co-workers [2]. By condensing 1,2-dihydro-7-methoxy-4 vinylnaphthalene with 3-methyl-3 pentene-1,2-dione and then demethylating and reducing the product, Dane succeeded in obtaining an isomer of estrone [3].



For the purpose of this synthesis Dane developed a method for the preparation of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) by condensation of ethynylmagnesium halide with 3,4-dihydro-6-methoxy-1(2H)-naphthalenone.

This method is referred to by Goldberg and Muller [4], Bockemuller [5], Anner and Miescher [6], and Heer and Miescher [7], who, however, do not describe their experiments on the preparation of the dihydromethoxyvinylnaphthalene I.

In 1948 Bachmann [8] modified this method, using iodides in place of bromides with benzene as solvent.

Our attempts to repeat the synthesis of 1,2-dihydro-7-methoxy-4-vinylnaphthalene by the procedure described have not been successful. It was found to be quite impossible to effect the condensation of 3,4-dihydro-6-methoxy--1(2H)-naphthalenone with acetylene by Dane's method, and Bachmann's method suffers from the defect that in the course of the distillation of the condensation products, even in a high vacuum (0.01 mm) the material completely resinifies. We have, therefore, developed a new method for the condensation of acetylene with aromatic ketones under pressure. We have observed that at a sufficiently low temperature (−70°) acetylene does not react at all with ethylmagnesium iodide; reaction proceeds at an appreciable rate only at temperatures above −30°. This observation forms the basis of the method we have developed for the condensation of 3,4-dihydro-6-methoxy 1(2H) naphthalenone with acetylene, which is described in detail in the experimental section. At −70° an ethereal solution of ethylmagnesium bromide (or iodide) will dissolve a large amount of acetylene, but no evolution of ethane is observed.

If the passage of acetylene is carried out at −20°, the reaction proceeds at an appreciable rate, and the ethane evolved rapidly develops a pressure in the reaction vessel which is considerably greater than the pressure of the acetylene itself.

It was found to be most satisfactory to saturate the ethereal solution of ethylmagnesium bromide with acetylene at −70° under a pressure of 2-3 atm, and then carry out the reaction at 0-10°; the pressure in the reaction vessel then rose to 20-30 atm. The "ethynylmagnesium bromide" obtained in this way was a semitransparent reddish-brown viscous mass, which was completely precipitated from ether at −70° and had the appearance of fruit-flavored ice cream. This is evidently the most active form of "ethynylmagnesium bromide", for when a complex of this form is obtained the yields of the reaction products are always greatest. "Ethynylmagnesium bromide" is readily soluble in toluene at temperatures above −4°, but below −4° the toluene solution separates into two layers. The lower layer, which contains the Iotsich complex, is a mobile liquid at temperatures above −20°, but below this temperature it gradually thickens, though it is able to form a fine emulsion with toluene even at −50° when agitated strongly. Th nature of our reaction products indicates that our Iotsich complex contained both ethynylmagnesium halide and ethynylbis[magnesium halide], in spite of the fact that the pressure of acetylene during its reaction with ethylmagnesium bromide attained 30 atm.

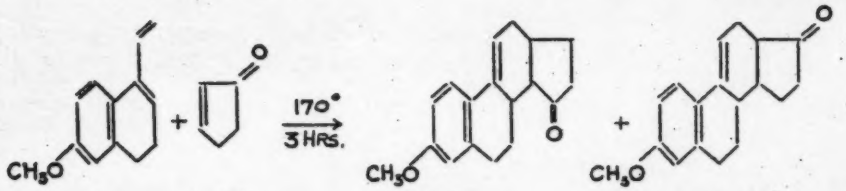
The work of Oddo [9], Iotsich [10], and Salkind and Rosenfeld [11] points to the formation of the monomagnesium compound, ethynylmagnesium halide; but in 1928 Grignard and co-workers [12] published a paper in which they suggested the presence of the equilibrium:

$$XMgC\equiv CMgX + HC\equiv CH \rightleftarrows 2XMgC\equiv CH$$

These authors showed that, when the acetylene Grignard reagent was saturated with acetylene in ether solution for four hours at 1 atm excess pressure at 45°, the subsequent introduction of carbon dioxide into the reaction mixture resulted in a 78% yield of propiolic acid.

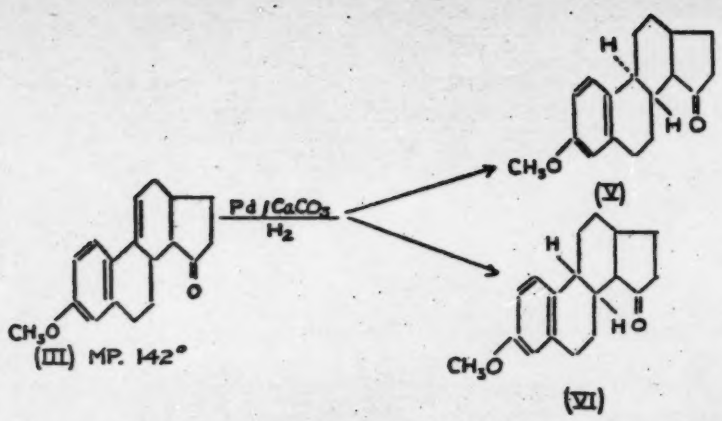
A toluene solution of the ketone was introduced at −50-60° into the Iotsich complex obtained as described above, and the reaction mixture was stirred at that temperature until a fine emulsion formed, after which it was warmed to the temperature at which the Iotsich complex was able to react with the ketone. In the case of the condensation of acetylene with 3,4-dihydro-6-methoxy-1(2H)-naphthalenone, decomposition of the complex must be effected with water only at −5-7°. When decomposition was effected with ammonium chloride a nonseparating emulsion was obtained, and decomposition with acid led to resinification of the reaction product.

By this procedure we effected the condensation with acetylene of acetophenone, 4'-methoxyacetophenone, and 3,4-dihydro-6-methoxy-1(2H)-naphthalenone, and obtained 1-methyl-1-phenyl-2-propyn-1-ol in 46% yield, 1-p-methoxyphenyl-1-methyl-2-propyn-1-ol in 30% yield, and 4-ethynyl-1,2-dihydro-7-methoxynaphthalene in 35% yield. In the course of the distillation of the product of the condensation of acetylene with 3,4-dihydro 6-methoxy-1(2H)-naphthalenone (1-ethynyl-1,2,3,4-tetrahydro-6-methoxy-1-naphthol) elimination of water occurred with formation of 4-ethynyl--1,2-dihydro-7-methoxynaphthalene. This substance was partially hydrogenated in presence of palladium on a calcium carbonate carrier, and was converted (by absorption of one molecule of hydrogen) into 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I). Condensation of this diene with 2-cyclopenten-1-one (II) gave a 35% yield of a mixture of two isomeric tetracyclic methoxy ketones (III and IV).

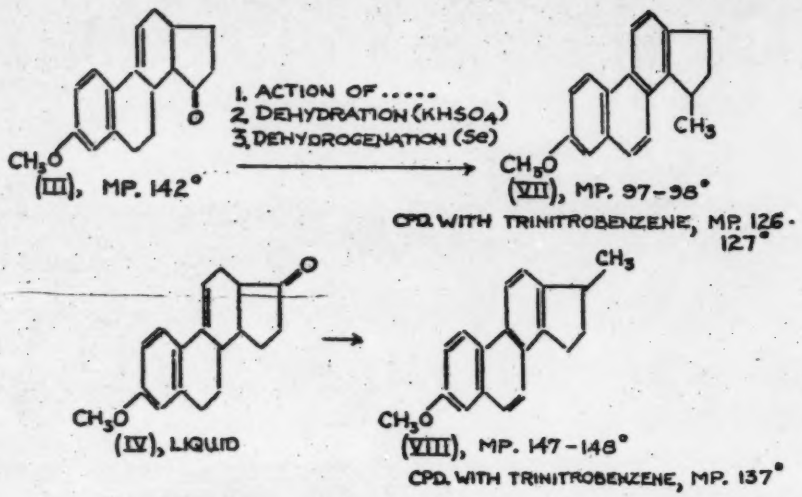


(I) (II) (III) (IV)

The methoxy ketone III was isolated as a crystalline substance, m.p. 142°, but its isomer (IV) was not completely purified and was obtained as light-yellow viscous noncrystallizing oil, b.p. 210-215° (0.05 mm). The crystalline product of m.p. 142° has been described previously by Dane and Eder [13], who erroneously assigned the formula IV to it (methoxy in the 17-position). The formation of the second methoxy ketone (IV) was not observed by Dane and Eder. Hydrogenation of the crystalline methoxy ketone III in presence of a palladium catalyst led to the formation of two isomeric tetracyclic methoxy ketones V and VI, which differ, in all probability, in the configurations of rings B and C:

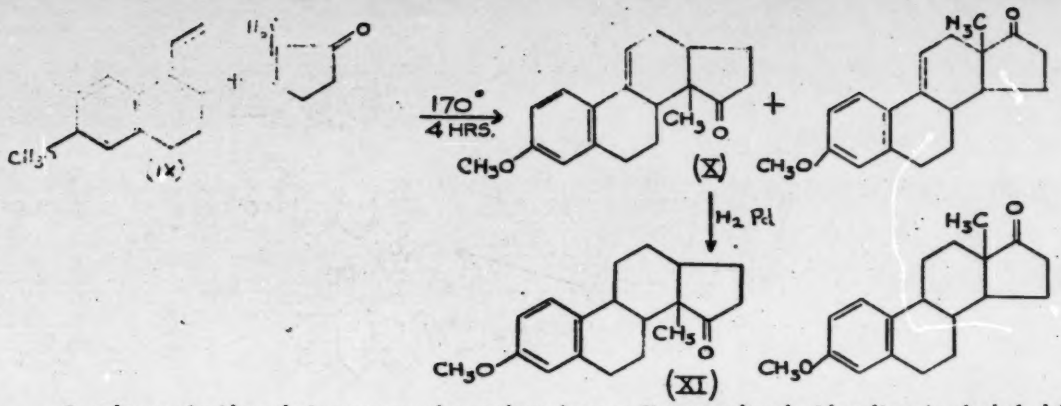


The structures of the methoxy ketones III and IV were proved by converting them into known cyclopenta[a]-phenanthrene derivatives (VII and VIII) according to the scheme given below.



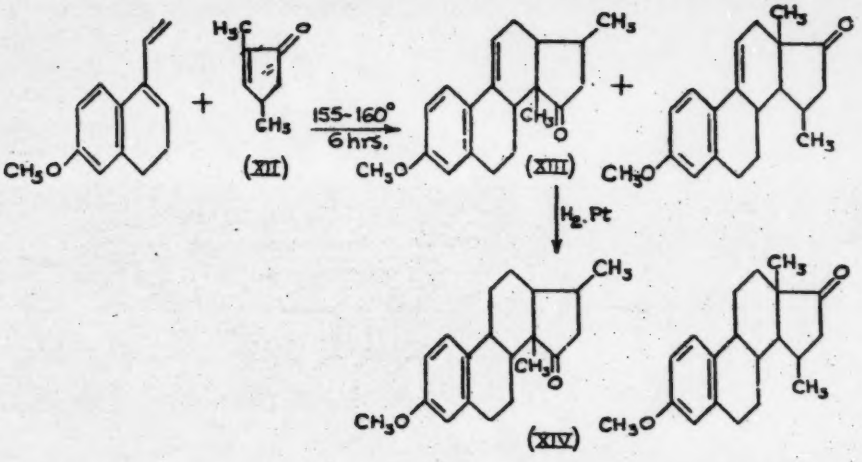
The melting points of the cyclopenta[a]phenanthrene derivatives VII and VIII so obtained, and also of their trinitrobenzene compounds, coincided with the data in the literature [14]. Thus, by the condensation of 1,2-dihydro--7-methoxy-4-vinylnaphthalene (I) with 2-cyclopenten-1-one (II), steroid ketones of both normal and "inverted" structure (keto groups in positions 17 and 15) are formed. As shown in previous communications [15], condensation of bicyclic dienes of the 1,2,3,4,4a,5,6,8a-octahydro-8-vinylnaphthalene type with α,β-unsaturated cyclic ketones yields tetracyclic steroid ketones solely or mainly of "inverted" structure (keto group in the 15-position).

When 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) is condensed with 2-methyl-2-cyclopenten-1-one (IX), the product (X) is again a mixture of isomeric tetracyclic methoxy ketones, and, when this is hydrogenated in presence of a platinum catalyst, one molecule of hydrogen is absorbed and a mixture of isomers of the methyl ether of estrone is formed (XI):

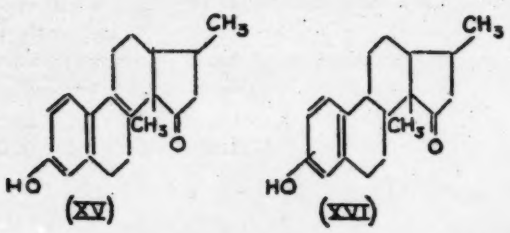


In order to elucidate their structure, the methoxy ketones X were reduced with sodium in alcohol, dehydrated, and dehydrogenated over selenium. As a result, a white crystalline substance, m.p. 136-136.3°, was isolated; its compound with trinitrobenzene melted at 147-148°.

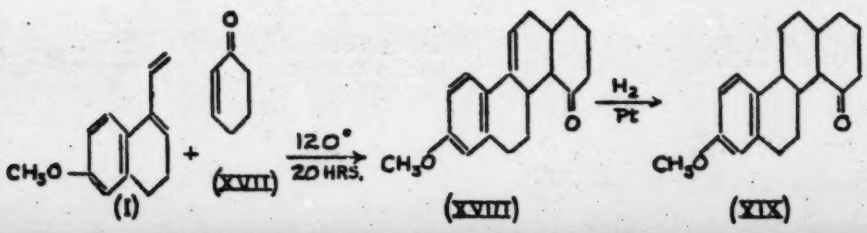
Condensation of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) with 2,4-dimethyl-2-cyclopenten-1-one (XII) yielded a mixture of isomeric tetracyclic ketones (XIII), which readily absorbed one molecule of hydrogen when hydrogenated, forming a mixture of isomers (spatial and structural) of the methyl ether of methylestrone (XIV):



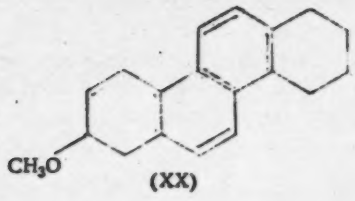
When demethylated with a mixture of glacial acetic and hydrobromic acids, the methoxy ketones XIII and XIV were converted into the corresponding hydroxy ketones XV and XVI, which are isomers of methylestrone:



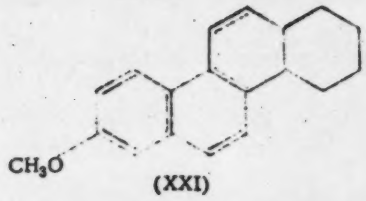
When 1,2-dihydro-7-methoxy-4-vinylnaphthalene was condensed with 2-cyclohexen-1-one (XVII), a 30% yield was obtained of a crystalline methoxy ketone, which probably had the structure XVIII:



This methoxy ketone, on being hydrogenated, absorbed one molecule of hydrogen and was converted into the crystalline methoxy ketone XIX. Attempts to demethylate the methoxy ketones XVIII and XIX with a mixture of glacial acetic and hydrobromic acids yielded crystalline products having much higher carbon contents than the original compounds. The analytical figures approximated to those for hydrogenated derivatives of methoxychrysene (XX and XXI):



(XX)



(XXI)

1-Methyl-1-phenyl-2-propyn-1-ol and 1-p-methoxyphenyl-1-methyl-2-propyn-1-ol, when partially hydrogenated in presence of palladium on a calcium carbonate carrier, absorbed one molecule of hydrogen and passed into the corresponding propenol compounds. In presence of potassium hydrogen sulfate, 1-methyl-1-phenyl-2-propen-1-ol lost one molecule of water and gave a 60% yield of 2-phenyl-1,3-butadiene. Under the same conditions, 1-p-methoxyphenyl-1-methyl-2-propen-1-ol also lost water, but at the same time polymerized, so that it was not found possible to prepare 2-p-methoxyphenyl-1,3-butadiene by this method. Whenmaleic anhydride was dissolved in an equimolecular amount of 2-phenyl-1,3-butadiene, there was a vigorous reaction with evolution of much heat, and the anhydride of 4-phenyl-4-cyclohexene-1,2-dicarboxylic acid was formed.

EXPERIMENTAL

1,2,3,4-Tetrahydro-6-methoxynaphthalene was prepared by methylation of 2-naphthol and hydrogenation of the 2-methoxynaphthalene obtained in presence of nickel and 1% of acetic acid in alcoholic solution in an autoclave at 140°. The α,β-unsaturated ketones were prepared by the method developed in our laboratory [16].

Oxidation of 1,2,3,4-Tetrahydro-6-methoxynaphthalene to 3,4-Dihydro-6-methoxy-1(2H)-naphthalenone. A solution of 140 g of chromic anhydride in 400 ml of glacial acetic acid and 50 ml of water was added over a period of five hours at 3° to a solution of 140 g of 1,2,3,4-tetrahydro-6-methoxynaphthalene in 800 ml of glacial acetic acid. The mixture was set aside overnight, and the acetic acid was then vacuum-distilled off at a bath temperature of 40-50°. The residual cake was dissolved in 500 ml of water (70°) and set aside overnight. The crystals (90 g) of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone that separated were filtered off, and the filtrate was extracted twice with ether (1 liter in all). The ether extract was dried with magnesium sulfate, and the residue after removal of ether was vacuum-fractionated, yielding 15 g of unchanged tetrahydromethoxynaphthalene, b.p. 83-85° at 1.5 mm, and 20 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone in the form of light-yellow crystals, b.p. 130-135° at 1 mm, m.p. 78-79°. The 90 g of crude product was also vacuum-distilled, yielding 16 g of unchanged tetrahydromethoxynaphthalene and 70 g of the dihydromethoxy-1(2H)-naphthalenone, the total yield of which was, therefore, 90 g (76.5% of the tetrahydromethoxynaphthalene that reacted.

Apparatus for Acetylenic Synthesis under Pressure. The apparatus in which the acetylenic syntheses under pressure were carried out consisted of a one-liter steel beaker having a flange; it could be screwed up to a cover, which was firmly clamped in a stand. A stirrer having a three-blade propeller passed through the center of the cover; it was driven with an electric motor and could be rotated at up to 400 r.p.m.. The cover was fitted also with tubes for the entrance and exit of gases, and with a precision manometer reading up to 40 atm in divisions of 0.2 atm. The apparatus was tested with nitrogen at 150 atm. Acetylene was obtained from a cylinder via a reduction valve, and it was passed through a steel washing vessel containing a solution of sodium hydrogen sulfite and through two steel columns filled with granulated caustic soda and calcium chloride respectively before finally passing to the apparatus.

4-Ethynyl-1,2-dihydro-7-methoxynaphthalene. An ethereal solution of ethylmagnesium bromide (20 g of magnesium, 95 g of ethyl bromide, and 200 ml of ether) was cooled to −70° and saturated for 40 minutes with acetylene at a pressure of 2.5 atm. The pressure in the 40-liter cylinder fell by 0.5 atm (absorption of about 20 liters of acetylene). The mixture was gradually warmed to 10° and stirred at that temperature for one hour (the pressure rose to 18 atm). The reaction beaker was again cooled to −70°, and the pressure, then fallen to 4 atm, was released. To the "ethynylmagnesium bromide" so obtained, which had precipitated on the bottom of the beaker in small lumps, a cooled (to −50°) solution of 20 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone in 500 ml of absolute toluene was added. The reaction mixture was stirred for 15 minutes at −70°, and was then gradually warmed to

10°, stirred at that temperature for one hour, and then stirred for a further 30 minutes at 45° (pressure 2-3 atm). The product was hydrolyzed by means of ice at −5°, the toluene-ether layer was poured off, and the residue was carefully washed with 200 ml of toluene. The solvent was vacuum-distilled from the united toluene-ether solution. The residue, which crystallized out in the distilling flask, was diluted with ether and filtered, and the residue on the filter was washed with a fresh portion of ether. The product was 7 g of di(3,4-dihydro-6-methoxy-1-naphthyl)acetylene, m.p. 176-177° (from benzene). Ether was removed from the filtrate in a current of nitrogen under reduced pressure, and then at the temperature of a boiling water bath residual solvent was removed, first with a water pump, and then with an oil pump. A two-stage pump was then brought into operation (0.04 mm), and the bath temperature was raised to 140°. Strong foaming occurred, and the bath temperature was maintained at the same level until foaming had practically stopped. The substance was then distilled, precautions being taken to avoid splashing over (all operations were performed in a current of nitrogen). The product was 7.2 g of 4-ethynyl-1,2-dihydro-7-methoxynaphthalene in the form of a light-yellow liquid, b.p. 118-125° (0.04-0.06 mm); n_D^{18} 1.6005; yield 34.5%.

	Found %:	C 83.30, 83.39; H 7.47, 7.43
$C_{13}H_{12}O$.	Calculated %:	C 84.75; H 6.52

As already stated by Bachmann, 4-ethynyl-1,2-dihydro-7-methoxynaphthalene is extremely unstable: within 30 minutes of distillation its yellow color had become appreciably more intense, and after standing 12 hours in the air it had become a thick reddish-brown sirup from which it was no longer possible to isolate anything by distillation. It is not recommended that this substance be redistilled, because of the great losses that occur as a result of polymerization. The analytical figures and the somewhat extended boiling range indicate that the 4-ethynyl-1,2-dihydro-7-methoxynaphthalene was contaminated with a small amount (5-10%) of the corresponding acetylenic tertiary alcohol, but when an attempt was made to eliminate water from these residues of tertiary alcohol by distillation of the substance over small amounts of potassium hydrogen sulfate the whole mass quickly polymerized into a hard glassy material, which began to distil in a high vacuum (about 0.01 mm) only at 320°. It is therefore necessary to use 4-ethynyl-1,2-dihydro-7-methoxynaphthalene very soon after its preparation and without further purification.

1,2-Dihydro-7-methoxy-4-vinylnaphthalene. Freshly prepared 4-ethynyl-1,2-dihydro-7-methoxynaphthalene (7.2 g) was hydrogenated in 20 ml of methanol in presence of palladium carried on calcium carbonate. In the course of 90 minutes 900 ml (20°, 752 mm) of hydrogen was absorbed, and the solution then no longer gave a positive test for acetylenic substances with an ammoniacal solution of silver oxide. Fractionation yielded 5.7 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I), b.p. 118-124° at 1.5 mm; n_D^{19} 1.5865. When this substance was ground for two minutes with maleic anhydride, an adduct was formed which, after careful washing with ether, melted at 201-202°, as stated in the literature.

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene with 2-Cyclopenten-1-one. A mixture of 3 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene and 8 g of 2-cyclopenten-1-one (II) (b.p. 34° at 7 mm; n_D^{20} 1.4745) was heated in a sealed tube for three hours at 170°. Vacuum fractionation yielded 6 g of unchanged cyclopentenone (b.p. 35° at 9 mm; n_D^{19} 1.4746) and 2.6 g of condensation product, b.p. 210-215° (0.06 mm). Repeated crystallization from alcohol yielded 1.5 g of the previously described crystalline methoxy ketone III, m.p. 142°, and 0.8 g of a liquid methoxy ketone (IV), b.p. 210-215° (0.5 mm).

	Found %:	C 80.62, 80.61; H 7.51, 7.59
$C_{18}H_{20}O_2$.	Calculated %:	C 80.55; H 7.46

The Tetracyclic Methoxy Ketones V and VI. The methoxy ketone III of m.p. 142° (0.7 g) was hydrogenated in 10 ml of methanol in presence of a palladium catalyst at 60°, 70 ml of hydrogen being absorbed in the course of 30 hours. Fractional crystallization from alcohol yielded 60 mg of a tetracyclic methoxy ketone (V or VI), m.p. 160-160.3°.

	Found %:	C 80.02, 79.80; H 8.32, 8.23
$C_{18}H_{22}O_2$.	Calculated %:	C 80.01; H 8.15

Also, 200 mg of the second isomer (methoxy ketone V or VI), m.p. 116-117°, was isolated.

	Found %:	C 79.90, 80.01; H 8.64, 8.67
$C_{18}H_{22}O_2$.	Calculated %:	C 80.01; H 8.15

Conversion of the Methoxy Ketone III into 16,17-Dihydro-3-methoxy-15-methyl-15H-cyclopenta[a]phenanthrene (VII). A solution of 0.4 g of the methoxy ketone III (m.p. 142°) in 20 ml of absolute ether was added under

vigorous stirring to an ethereal solution of methylmagnesium iodide prepared from 0.5 g of magnesium, 3.5 g of methyl iodide, and 40 ml of absolute ether. The mixture was boiled for 30 minutes, treated with 4% hydrochloric acid (17 ml), and extracted with ether. The extract was dried with magnesium sulfate, and the residue after removal of the ether was mixed with 0.5 g of freshly calcined potassium hydrogen sulfate; the mixture was heated in a bath at 180-190° until water ceased to separate (two hours). The product was extracted with ether, and the extract was dried with magnesium sulfate and vacuum-distilled, yielding 0.3 g of a colorless oil, b.p. 190-202° (0.1 mm). Scratching with a rod caused complete solidification (m.p. 88° [from alcohol]). A mixture of 0.28 g of this substance and 0.5 g of selenium was heated in a sealed tube for six hours at 300°. When the mass cooled, complete solidification occurred. The substance was dissolved in hot benzene, filtered three times to remove selenium, and, after removal of benzene, vacuum-distilled: b.p. 160-180° (0.1 mm). The distilled substance was recrystallized: once from a mixture of benzene and alcohol (1:4), and four times from alcohol. The product was 100 mg of 16,17-dihydro-3-methoxy-15-methyl-15H-cyclopenta[a]phenanthrene (VII), m.p. 97-98°; its compound with trinitrobenzene melted at 126-127° (the literature [16] gives 98° and 129° respectively).

Conversion of the Methoxy Ketone IV into 16,17-Dihydro-3-methoxy-17-methyl-15H-cyclopenta[a]phenanthrene (VIII). An ethereal solution of 1.2 g of the methoxy ketone IV (b.p. 210-215° at 0.05 mm) was added under stirring to an ethereal solution of methylmagnesium iodide prepared from 0.5 g of magnesium, 3.5 g of methyl iodide, and 40 ml of absolute ether. The organomagnesium complex was precipitated on the bottom of the flask. The mixture was stirred for one hour at 40°, and then treated first with water (2 ml), and then with 4% hydrochloric acid (17 ml). The product was extracted with ether, and the ether extract was dried with potassium carbonate. The ether was driven off, and the residue was heated with 0.5 g of potassium hydrogen sulfate for two hours at 170° under reduced pressure (8 mm). The dehydration product was extracted with ether, and the ether extract was washed with sodium bicarbonate solution, dried with magnesium sulfate, and vacuum-distilled, yielding 0.7 g of a light-yellow oil, b.p. 180-200° at 0.06 mm, which was heated with 0.5 g of selenium in a sealed tube for three hours at 300-320°. On cooling the substance solidified completely. When the tube was opened an appreciable pressure of hydrogen selenide was noted. The crystalline solid was dissolved in hot benzene, and the benzene solution was diluted with an equal volume of alcohol; suspended selenium was carefully filtered off. When the filtrate was cooled, a voluminous crystalline precipitate appeared. Four recrystallizations from alcohol yielded 200 mg of 16,17-dihydro-3-methoxy-17-methyl-15H-cyclopenta[a]phenanthrene (VIII), m.p. 147-148°; compound with trinitrobenzene, m.p. 136.5-137° (the literature [16] gives 147.5-148° and 137° respectively).

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene (I) with 2-Methyl-2-cyclopenten-1-one (IX). A solution of 1 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) in 10 g of 2-methyl-2-cyclopenten-1-one (IX) (b.p. 62-65° at 23 mm; n_D^{20} 1.4795) was heated for four hours in a sealed glass tube at 170°. After removal of methylcyclopentenone and an intermediate fraction (0.6 g, b.p. 110-140° at 2 mm) by distillation, 0.6 g of a mixture of steroid methoxy ketones (X) was isolated as a light-yellow glassy substance, b.p. 220-222° at 2 mm.

	Found %:	C 80.32, 80.04; H 8.12, 8.01
$C_{19}H_{22}O_2$.	Calculated %:	C 80.84; H 7.80

Chromatographic separation on aluminum oxide was carried out with 1 g of this product, and elution with petroleum ether yielded 0.3 g of material, which was dissolved in 15 ml of alcohol and reduced with sodium (1 g) at 78°. The mixture was neutralized with 4 ml of concentrated hydrochloric acid, the alcohol was distilled off, and the substance was extracted with ether. The ether extract was dried with magnesium sulfate, and the residue after removal of ether was heated for one hour with 0.5 g of freshly calcined potassium hydrogen sulfate at 180°. The product was extracted with ether, and the ether extract was washed with sodium bicarbonate solution, dried with magnesium sulfate, and vacuum-distilled, yielding 0.2 g of a light-yellow oil, b.p. 180-195° (0.2 mm). This dehydrogenation product was heated with 93 mg of selenium in a sealed tube at 320-330° for seven hours. The substance was freed from resinous contamination by chromatography on aluminum oxide and recrystallized several times from alcohol, yielding 50 mg of colorless crystals, m.p. 136-136.3°.

	Found %:	C 86.58, 86.54; H 6.49, 6.35
$C_{19}H_{18}O$.	Calculated %:	C 87.02; H 6.87

Its compound with trinitrobenzene melted at 147-148° (from alcohol).

Hydrogenation of the Steroid Methoxy Ketones X. The substance (0.27 g) was hydrogenated in 20 ml of alcohol in presence of a platinum catalyst; 22 ml of hydrogen (one molecule) was absorbed. The alcohol was driven off, and the substance was vacuum-distilled, yielding 220 mg of a light-yellow oil, b.p. 199-203° at 0.1 mm. The product was a mixture of isomers (XI) of the methyl ether of estrone.

	Found %:	C 80.42, 80.26; H 8.01, 8.03
$C_{19}H_{24}O_2$.	Calculated %:	C 80.20; H 8.44

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene (I) with 2,4-Dimethyl-2-cyclopenten-1-one (XII). A mixture of 2.7 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) and 8 g of 2,4-dimethyl-2-cyclopenten-1-one (XII) was heated in a sealed tube for six hours at 155-160°. Unchanged dimethylcyclopentenone was driven off under reduced pressure, and fractionation of the residue yielded 0.8 g of a mixture of the steroid methoxy ketones (XIII) as very viscous yellow oil, b.p. 205-208° (0.1 mm).

	Found %:	C 80.04, 80.21; H 8.01, 8.16
$C_{20}H_{26}O_2$.	Calculated %:	C 81.04; H 8.1

Demethylation of the Steroid Methoxy Ketones XIII. A mixture of 0.4 g of material, 5 ml of glacial acetic acid, and 3 ml of 48% hydrobromic acid was heated under reflux for six hours at a bath temperature of 120°. The acids were driven off under reduced pressure, and the residue was dissolved in 20 ml of 3% caustic soda. The alkaline solution was extracted with ether and acidified with hydrochloric acid. A mixture of the steroid ketones XV (0.2 g) was isolated in the form of a yellow glassy mass, b.p. about 215-220° (0.03 mm).

	Found %:	C 81.36, 81.31; H 7.67, 7.77
$C_{19}H_{22}O_2$.	Calculated %:	C 80.84; H 7.80

Hydrogenation of the Steroid Ketones XIII. A solution of 0.75 g of the substance in 20 ml of alcohol was hydrogenated in presence of platinum, one molecule of hydrogen (64 ml, 20°, 745 mm) being absorbed in two hours. Vacuum fractionation yielded 0.65 g of the mixture of steroid methoxy ketones XIV in the form of a colorless oil, b.p. 195-200° (0.1 mm).

	Found %:	C 80.23, 80.33; H 8.61, 8.81
$C_{20}H_{26}O_2$.	Calculated %:	C 80.45; H 8.72

Demethylation of the Steroid Methoxy Ketones XIV. A mixture of 0.23 g of the substance, 3 ml of glacial acetic acid, and 1.5 ml of 48% hydrobromic acid was boiled for three hours, the bath temperature being 120-125°. The acids were distilled off under reduced pressure, and the residue was dissolved in 10 ml of 5% caustic potash. The alkaline solution was washed with ether and acidified with hydrochloric acid. An amorphous solid mass was precipitated, and this, after being filtered off, washed with water, and dried, was vacuum-distilled, yielding 0.17 g of the mixture of steroid hydroxy ketones XVI in the form of light-yellow glassy substance, b.p. 215-220° (0.03 mm).

	Found %:	C 80.40, 80.17; H 8.54, 8.64
$C_{19}H_{24}O_2$.	Calculated %:	C 80.20; H 8.44

Condensation of 1,2-Dihydro-7-methoxy-4-vinylnaphthalene (I) with 2-Cyclohexen-1-one (XVII). A solution of 4 g of 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I) in 12 ml of 2-cyclohexen-1-one (XVII), b.p. 161°; n_D^{20} 1.4860 was heated in a sealed tube for 20 hours at 120°. The cyclohexeneone was distilled off under reduced pressure, and was followed by 2 g of a substance boiling over the range 100-170° at 1 mm. Alcohol (20 ml) was added to the residue in the flask, and the solution was set aside for a day. The crystals that separated were filtered off. Recrystallization from alcohol yielded 2 g of the tetracyclic methoxy ketone XVIII in the form of glistening white crystals, m.p. 132°.

	Found %:	C 80.80, 81.09; H 7.93, 7.74
$C_{19}H_{22}O_2$.	Calculated %:	C 80.84; H 7.80

Hydrogenation of the Methoxy Ketones XVIII. The substance XVIII of m.p. 132° (0.3 g) was hydrogenated in 20 ml of alcohol in presence of a palladium catalyst, first at room temperature, and then at 70°; 23 ml of hydrogen was absorbed. The product was distilled off at 220-222° (0.1 mm), left for a week to crystallize, and then recrystallized from alcohol. The product was 70 mg of the tetracyclic methoxy ketone XIX in the form of white crystals, m.p. 147° (from alcohol).

	Found %:	C 80.05, 79.81; H 9.24, 9.27
$C_{19}H_{24}O_2$.	Calculated %:	C 80.20; H 8.44

Demethylation of the Methoxy Ketones XVIII. A mixture of 0.1 g of the substance, 6 ml of glacial acetic acid, and 3 ml of 48% hydrobromic acid was boiled for three hours (bath temperature 120°). When the mixture was cool, crystals came down, and these were separated and recrystallized from 60% alcohol, yielding 50 mg of 1,2,3,4-tetrahydro-8-methoxychrysene (XX) in the form of gray crystals melting at 183° (from 60% alcohol), insoluble in dilute alkali.

	Found %:	C 86.91; H 7.48
$C_{19}H_{18}O$.	Calculated %:	C 87.05; H 6.88

Demethylation of the Methoxy Ketones XIX. A mixture of 40 mg of the substance, 2 ml of glacial acetic acid, and 1 ml of 48% hydrobromic acid was boiled for 90 minutes (bath temperature 120-130°) When the mixture was cooled, crystals separated, and these, after recrystallization from 70% acetic acid, washing with water, and drying in a vacuum desiccator over sulfuric acid, melted at 219-220°. In this way 30 mg of pinkish crystals were obtained, evidently of 1,2,3,4,4a,12a-hexahydro-8-methoxychrysene (XXI); they were insoluble in dilute alkali.

	Found %:	C 86.32, 86.37; H 6.46, 6.63
$C_{19}H_{20}O$.	Calculated %:	C 86.40; H 7.57

SUMMARY

1. A new method has been developed for the preparation of ethynylmagnesium bromide under pressure, and it has been condensed with aromatic and hydrogenated aromatic ketones. In this way the synthesis has been effected in 30-46% yield of 1-methyl-1-phenyl-2-propyn-1-ol, 1-p-methoxyphenyl-1-methyl-2-propyn-1-ol, and 4-ethynyl-1,2-dihydro-7-methoxynaphthalene.

2. The last compound has been selectively hydrogenated to 1,2-dihydro-7-methoxy-4-vinylnaphthalene (I), which has been condensed with 2-cyclopenten-1-one (II), 2-methyl-2-cyclopenten-1-one (IX), 2,4-dimethyl-2-cyclopenten-1-one (XII) and 2-cyclohexen-1-one (XVII). In this way a number of tetracyclic ketones related to estrone have been synthesized, and in two cases their structures have been proved.

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** See Consultants Bureau Translation, page 799.
*** See Consultants Bureau Translation, page 787.

STABILITY OF SKELETAL NICKEL CATALYST AT ELEVATED TEMPERATURE

L. Kh. Freidlin and K. G. Rudneva

The skeletal (i.e., Raney) nickel catalyst has found application mainly in low-temperature hydrogenation reactions, and is scarcely used for processes, e. g. dehydrogenation, requiring higher temperatures. The limited field of application of this catalyst is evidently the result of its inadequate thermal stability.

The available data on the thermal dehydrogenation and thermal stability of the skeletal nickel catalyst are contradictory. According to Aubry [1], when Raney nickel is boiled in concentrated sodium or potassium carbonate solution for a long time, much of its adsorbed hydrogen is removed, and aggregation of its particles occurs; the catalyst becomes darker in color, changes in specific volume, and partially loses its activity. Bougault and coworkers [2] have shown that, in a vacuum, dehydrogenation of skeletal nickel begins at 100° and is complete at 250°. Mozingo [3] effected the removal of hydrogen from skeletal nickel suspended in a high-boiling organic substance (dibutyl phthalate) by passage of carbon dioxide at 220°. Schwab and Zorn [4] observed that, when skeletal nickel was kept in a high vacuum for five days at room temperature, its catalytic activity was greatly reduced. We gain the impression that the skeletal nickel catalyst is of low thermal stability and is already fully dehydrogenated and deactivated at temperatures of 200-250°.

Other facts, however, point to the appreciable stability of this catalyst, even at elevated temperatures: Rutovsky and coworkers [5] have dehydrogenated borneol to camphor at 240° in its presence, and Rappoport [6] has used it in the dehydrogenation of cyclohexane and methylcyclohexane

It is also not clear whether the deactivation of this catalyst at high temperature is due to recrystallization or to the effect of other factors.

As Eucken has shown [7], the specific surface of a skeletal nickel catalyst falls only slowly during the activation process, even when a comparatively high temperature is used:

Temperature of catalyst activation (°C)	25	200	370
Specific surface (sq. m/g)	22.9	18.5	16.4

It may therefore be supposed that sintering is not the main cause of the deactivation of this catalyst under the usual conditions of the hydrogenation or dehydrogenation process.

It has recently been established that the skeletal nickel catalyst is a metal-hydrogen system. Hydrogen is an essential component of its active surface. Hence, not only blocking of the active surface, but also dehydrogenation of the catalyst must constitute an important deactivation process.

In view of these considerations we have investigated the thermal stability of a skeletal nickel catalyst. The results show that the catalyst is very stable in absence of hydrogenatable substances. At 300° its activity was unaltered, and only when baked at 400° did its activity begin to fall; but even after it was baked at 500° and 570° it still had a considerable activity and retained a large amount of hydrogen. Under vacuum conditions the catalyst was deactivated at a lower temperature, and the dehydrogenation and deactivation of Raney nickel observed by some investigators at 200-250° can be explained by the effect of the vacuum and of such contaminants as sodium and potassium carbonates and dibutyl phthalate. On the other hand, borneol and cyclohexane and their dehydrogenation products have little effect on the activity of the catalyst.

The apparent contradictions in the facts given above are therefore explained: the stability of the skeletal catalyst is affected mainly not by the temperature, but by the nature of the process and the chemical nature of the substances whose reactions are being accelerated by the catalyst.

EXPERIMENTAL

Thermal Deactivation of Skeletal Nickel Catalyst in a Current of Nitrogen

The catalyst was prepared by treating a 50% Ni–Al alloy with 20% caustic soda at 100°. The active catalyst (15 g) in the form of a paste was placed in a quartz tube, which was heated in an electric furnace fitted with a thermoregulator. A current of nitrogen freed from oxygen and moisture by means of sodium dithionite and sulfuric acid respectively was passed continuously during the experiment at 3.5 l./hour. The preliminary heating of the furnace to the temperature of the experiment did not, as a rule, take more than 30-40 minutes, and it was not included in the time given for the duration of the experiment. At the end of the experiment, the catalyst was cooled to room temperature and then transferred in a current of nitrogen to below the surface of water in a suitable vessel.

The activities of the original and thermally deactivated samples of catalyst were estimated from measurements of the rate of hydrogen absorption in the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20°.

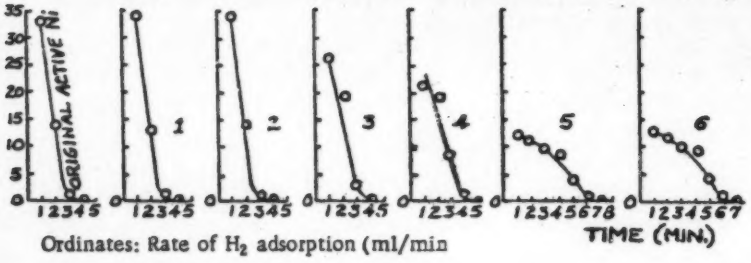
TABLE 1
Thermal Deactivation of a Skeletal Nickel Catalyst in a Current of Nitrogen

Temperature (°C)	Duration of expt. (hr)	Activity of 1 g of catalyst in the first 4 min. of the hydrogenation of phenyl vinyl ether (rate of hydrogen absorption in ml/min)	Amount of hydrogen found in 1 g of catalyst (ml)
200	2	33.6–12.8–1.0 –0.2	–
300	2	33.7–13.5–0.9 –0.2	80
300	4	29.4–16.5–2.0 –0.5	–
400	2	26.2–18.3–3.2 –0.2	–
500	2	20.9–18.9–8.7 –0.3	63
570	2	12.4–11.1–9.7 –7.3	54
570	6	12.6–11.5–10.1–8.9	–
Original active nickel		33.0–13.7–1.2 –0.2	179

Before the activity determination, the catalyst was saturated with hydrogen for 15 minutes. A determination was made also of the residual hydrogen in the catalyst by treating it with excess of a 3% solution of p-benzoquinone in dioxane in an atmosphere of nitrogen for one hour at 60°.

It follows from Table 1 and Fig. 1 and 2 that the skeletal nickel catalyst preserved its original activity after a two-hour heating at 300°. After two hours at 400°, the activity of the catalyst fell appreciably. Considerably greater deactivation occurred at 500°, and it was still greater at 570°.

These results show that only at 400° and above does appreciable deactivation occur. The effect increases with rise in temperature, but even after being baked at 570° the catalyst still retains much of its activity and



Ordinates: Rate of H_2 adsorption (ml/min)

Fig. 1. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a current of nitrogen: 1) at 200°, 2 hr; 2) at 300°, 2 hr; 3) at 400°, 2 hr; 4) at 500°, 2 hr; 5) at 570°, 2 hr; 6) at 570°, 6 hr.

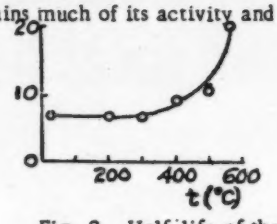


Fig. 2. Half-life of the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a current of nitrogen for two hours at a temperature in the range 200-570°.

TABLE 2
Thermal Deactivation of a Skeletal Nickel Catalyst in a Vacuum

Temperature (°C)	Duration of expt. (hr)	Activity of 1 g of catalyst in the first 4 min. of the hydrogenation of phenyl vinyl ether (rate of hydrogen absorption in ml/min)	Amt. of hydrogen found in 1 g of catalyst (ml)
300	2	17.2–16.3–12.7–2.8	52
400	2	15.3–14.3–11.8–5.3	40
Original active nickel		26.8–14.6– 2.2–0.7	207

contains an appreciable amount of hydrogen. Increase of the duration of thermal treatment at 570° from two to six hours has no effect on the reduction in the activity of the catalyst.

It is necessary to draw attention to another interesting fact. It has been found previously that about 70% of all the hydrogen contained in the catalyst is a constituent part of its active surface, and only about 30% of the hydrogen can be removed without effect on the activity of the catalyst [9]. In the experiments on thermal deactivation in a current of nitrogen at 300°, the catalyst was found to contain about 50% of the amount of hydrogen normally found in an untreated sample of catalyst, and yet the activity of the catalyst was fully retained. The activating effect of hydrogen in a catalyst that has been submitted to thermal treatment is therefore considerably higher than in a freshly prepared catalyst.

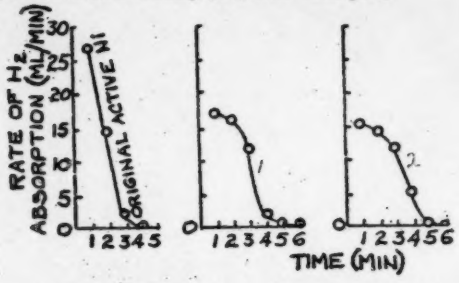


Fig. 3. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a vacuum for two hours: 1) at 300°; 2) at 400°.

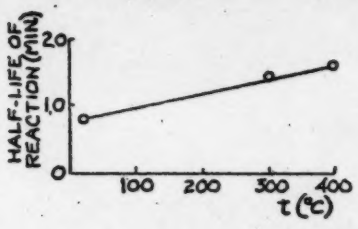


Fig. 4. Half-life of the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel dehydrogenated in a vacuum for two hours at 300° and 400°.

Thermal Deactivation of Skeletal Nickel Catalyst in a Vacuum

Active catalyst (10 g) in the form of a paste was transferred in a current of hydrogen to a quartz tube. One end of the tube was securely stoppered, and the other was attached to a vacuum pump that maintained a pressure of 1-5 mm Hg in the system. In other respects the experiment was performed like those on thermal deactivation in a current of nitrogen. The results obtained are given in Table 2 and represented in Figs. 3 and 4. It follows from Table 2 and Figs. 3 and 4 that in the thermal-deactivation treatments in a vacuum at 300° and 400° the activity and hydrogen content of the catalyst fall more rapidly than in treatments carried out in a current of nitrogen.

SUMMARY

1. An investigation has been made of the thermal deactivation of a skeletal nickel catalyst in a current of nitrogen and in a vacuum.

2. It has been shown that a skeletal nickel catalyst is of good stability to baking in a current of nitrogen in absence of organic substances. Its activity is not reduced by a two-hour baking at 300°; deactivation and dehydrogenation of the catalyst become appreciable only at 400° and higher, and they then become more and more marked as the temperature is raised.

3. When the catalyst is heated in a vacuum, its activity falls more rapidly than when treatment is carried out in a current of nitrogen.

4. The results obtained support our hypothesis that the most important cause of the loss in the activity of skeletal nickel catalyst under the usual conditions of hydrogenation is not recrystallization, but destruction of the active surface by chemical dehydrogenation and blocking.

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MACROMOLECULAR COMPOUNDS

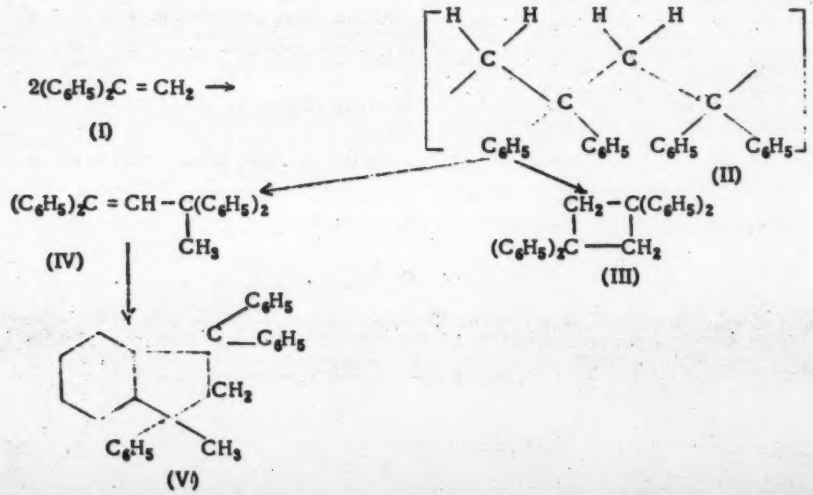
COMMUNICATION 60. ROLE OF STEREOCHEMICAL FACTORS IN THE POLYMERIZATION PROCESS

V. V. Korshak and N. G. Matveeva

In previous communications [1-5] we have given the results of investigations on the effect of substituents in the ethylene molecule on its polymerizability. On the basis of the behavior of halogen-substituted ethylenes [1], certain 1,1-diarylethylenes [2], ar-substituted styrenes [3, 4] and α-methylstyrenes [5], we have succeeded in proving the correctness of the hypothesis that we have advanced, according to which the polymerizability of substituted ethylenes is determined by the number and sizes of the substituents [6-8].

Stereochemical factors are therefore of the greatest importance in the large group of tri- and tetra-substituted ethylenes, since it is in these that steric hindrance due to the substituents is of most significance [1]. We have, however, succeeded in showing that even for mono- and di-substituted ethylenes stereochemical factors are extremely important. First of all, we have unsymmetrical disubstituted ethylenes such as 2,6-dimethoxy-α-methylstyrene [5] and 4-tert-butyl-α,2,6-trimethylstyrene [5], which have completely lost their tendency to polymerize owing to the complete screening and blocking of the double bond by the substituents. The same sort of phenomenon is found in monosubstituted ethylenes when the substituent is sufficiently ramified and so able to block the vinyl group. Examples of such compounds are 2,4,6-trimethylstyrene [9] and 4-tert-butyl-2,6-dimethylstyrene [3], which have almost lost their ability to undergo radical polymerization, while preserving their ability to undergo ionic polymerization; and finally 2,4,6-tris(trifluoromethyl)styrene, which has completely lost the ability to undergo both radical and ionic polymerization [10]. Steric hindrance, therefore, may play an important role in the behavior of ethylenes of any degree of substitution, from tetra- to di-substituted, and may often result in complete loss of the ability to undergo polymerization.

We meet another mode of action of stereochemical factors in the case of ethylenes having two large substituents. A well-studied example of this kind is 1,1-diphenylethylene: it is well known that it can form a dimer, but no one has yet succeeded in obtaining a polymer having a degree of polymerization of greater than 2, although attempts have been made by Lebedev [11], Belov [12], one of us with Samplavskaya [13], and other investigators [14]. An explanation of this fact involving stereochemical factors has been given [13]: owing to the large size of the phenyl groups, great strains arise in the dimer formed in the first stage of the reaction which lead to the immediate isomerization of the dimer (II) either into 1,1,3,3-tetraphenylcyclobutane (III), or into 1,1,3,3-tetraphenyl-1-butene (IV), which will be readily converted further into 1-methyl-1,3,3-triphenylindan (V), as shown in the scheme given below:



In this case, therefore, stereochemical factors play an important part in the actual polymerization process; they lead to the early rupture of the chain [7]. There is reason to suppose that this is not an isolated case, for it is known that many monomers having two substituents in the 1,2-positions tend to form dimers; these include stilbene [15], 1,2-dichloroethylene [16], and cinnamic acid [17]. The mechanism whereby the chain is terminated is probably similar for these compounds.

It may be supposed that stereochemical factors, apart from having effects of these two types, have some influence on the courses of the separate elementary reactions of the polymerization process, thus determining a number of the characteristics of the process and the structure of the polymer that have been previously attributed entirely to polar effects—primarily, to the polarization of the monomer.

The elucidation of all the details and the building up of a complete picture of stereochemical effects in polymerization processes comprise a task demanding much investigational work and a considerable period of time. Even now, however, it is possible to present certain sides of the question sufficiently clearly and with reasonable confidence in their accuracy.

In this paper we shall consider the question of the extent to which stereochemical factors determine the manner in which the monomer residues are arranged along the macromolecule of the polymer. It has been generally considered that the directions in which the monomer residues are disposed in the polymer chain are determined by the polarization of the double bond, as a result of which the residues take up definite directions along the chain.

Investigations by many workers have shown that monomer molecules take up a head-to-tail arrangement in the polymer macromolecule. Thus, Staudinger and Steinhofer [18] and Midgeley [19] have shown that the polystyrene molecule has this structure, its formula being:

$$\cdots -CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}- \cdots$$

The structure of polyvinyl acetate has been studied by Staudinger and Schwalbach [20], Marvel and Denoon [21], Korshak and Zamyatina [22], and Losev and Trostyanskaya [23], and they have found that both polyvinyl acetate itself, and also polyvinyl alcohol prepared from it, are built up in the same way, the formula of the latter being as follows:

$$\cdots -CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}- \cdots$$

Chalmers [24] and Korshak and Zamyatina [25] have established that poly[alkyl vinyl ethers] have the following structure:

$$\cdots -CH_2-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OR}{\underset{|}{CH}}- \cdots$$

The structure of polyvinyl chloride has been studied by Staudinger and Schneiders [26], Marvel, Sampel, and Roy [27], and Korshak and Zamyatina [28]; and the structure of polyvinyl bromide has been studied by Ostromyslensky [29] and Korshak, Samplavskaya, and Dovolskaya [30]. The identity of the results obtained in the two cases permits us to conclude that all polyvinyl halides have the same structure, which is expressed by the formula:

$$\cdots -CH_2-CHX-CH_2-CHX-CH_2-CHX- \cdots$$

We may therefore conclude that the general law for the structure of polymers is not that the arrangement of monomer residues in the polymer macromolecule is an irregular one, but, on the contrary, that it is regular, and may be represented in general for polymers of vinyl compounds by the formula:

$$\cdots -CH_2-CHX-CH_2-CHX-CH_2-CHX- \cdots$$

and for polymers of vinylidene compounds by the formula:

$$\cdots -CH_2-CX_2-CH_2-CX_2-CH_2-CX_2- \cdots$$

The explanation advanced for this is that the double bond of the monomer is polarized, so that each carbon atom has a charge:

$$\overset{\ominus}{CH_2} = \overset{\oplus}{CHX},$$

and the monomer residues have to unite through oppositely charged carbon atoms [31]. Recently, this concept has been further supplemented by the idea of the positive or negative charge of the double bond, which is regarded as affecting the ease with which different monomers combine in copolymerization [32].

We consider that these concepts should be supplemented by taking into account the effect of the stereochemistry of the monomer on the polymerization process. In principle, the uniting of two molecules, as we have already noted, can proceed in two ways: head to head, or head to tail. In practice, only one method is realized: head to tail. This method of uniting monomer molecules is to be preferred also from the stereochemical point of view: it is only necessary to compare the two methods of uniting monomer residues, in the case, for example, of the polymerization of vinylidene chloride, for the difference between them to become clear. In the case of head-to-head union, two vinylidene chloride molecules will combine as follows:

$$CH_2 = CCl_2 + CCl_2 = CH_2$$

and yield a macromolecule of the following structure:

$$\cdots -CH_2-CCl_2-CCl_2-CH_2- \cdots$$

In the case of head-to-tail union, the positions of the uniting molecules will be different, and the structure of the polymer will also be different:

$$CH_2 = CCl_2 + CH_2 = CCl_2$$

$$\cdots -CH_2-CCl_2-CH_2-CCl_2- \cdots$$

In the first case, therefore, the two groups $= CCl_2 + CCl_2 =$, have to unite, which is precisely analogous to the case, which we have investigated, of the polymerization of tetrachloroethylene, which is quite unable to polymerize, as we have already established [1]. The source of the inertness of tetrachloroethylene lies, as we have shown, in the great steric obstacles that are met in the union of two $= CCl_2$ groups. These great steric obstacles make it impossible for tetrachloroethylene to polymerize, and they also do not permit vinylidene chloride molecules to unite in such a stereochemically difficult manner.

In the second case it is the groups $= CH_2$ and $= CCl_2$ that have to unite, and this, of course, does not demand the surmounting of such great steric obstacles; it should therefore proceed with considerably greater ease. In the actual polymerization, therefore, the vinylidene chloride molecules unite in the second way. It will be clear that the activation energy in the first case will be much greater than in the second, in which the obstacles to be surmounted are not so great.

We meet similar behavior in practically all monomers, which are generally vinyl or vinylidene compounds. Thus, also in the case of vinyl compounds we find great stereochemical differences between the two possible modes of union of monomer molecules. In the case of vinyl chloride, for example, in the first case the groups = CHCl + + CHCl = must unite, but in the second the groups $= CHCl + CH_2 =$. It will be clear that in the first case the steric hindrance will be much greater than in the second, and this fact determines the method of union that is observed in practice. In the first case we see the same picture as that presented by dichloroethylene, which, as is well known, does not polymerize, as a result, we consider, of steric-hindrance effects, together with other causes relating to polar effects.

SUMMARY

1. The part played by stereochemical factors in polymerization processes has been examined, and it has been shown that they may play an important part, not only in the first stages of the reaction, which determine the existence or nonexistence of polymerizability, but also in the succeeding stages of the process.

2. It has been shown that in the polymerization process stereochemical factors can cause the chain to be terminated at the dimer stage; this is a consequence of the great strains that may arise in the molecule on account of the presence of bulky substituents.

3. It has been shown that stereochemical factors play an important part, together with polar effects, in determining the directions in which the monomer molecules unite when forming the polymer chain, the directions being determined by the magnitudes of the steric hindrance effects operating for the two different ways of building up the macromolecule.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 63. POLYESTERS OF 1,20-EICOSANEDIOL

V. V. Korshak and S. V. Vinogradova

Up to now only isolated attempts have been made to determine how the physical properties of a polymer depend on the length of the structural unit, i.e., of the monomer. Hill and Walker [1], for example, give a graph showing the variation in the melting points of polyureas, polyamides, polyurethans, and polyesters with the length of the structural unit for compounds having units of 14-26 atoms. They give also a graph for the variation in the melting points of some polyesters of 1,10-decanediol, but some points are missing. Their data on polyamides are also incomplete. Moreover, Hill and Walker, in compiling their review article, have made use of results, which, being obtained by various workers under various conditions, frequently differ greatly from one another.

We have therefore undertaken the task of preparing a number of polyesters under identical conditions from a given diol and various dicarboxylic acids. With this object we have prepared polyesters of 1,20-eicosanediol and the dicarboxylic acids from oxalic to sebacic. In the case of oxalic and malonic acids, we used their esters—diethyl oxalate and diisopropyl malonate—as starting materials, because one of us with Rogozhin has shown that

TABLE

Polyester	Formula	No. of C atoms in acid	No. of C atoms in unit	M. p. of polyester (°C)
Polyeicosamethylene oxalate . . .	$[-O(CH_2)_{20}OOC-CO-]_x$	2	24	88-90
Polyeicosamethylene malonate . .	$[-O(CH_2)_{20}OOC(CH_2)CO-]_x$	3	25	67-69
Polyeicosamethylene succinate . .	$[-O(CH_2)_{20}OOC(CH_2)_2CO-]_x$	4	26	86-89
Polyeicosamethylene glutarate . .	$[-O(CH_2)_{20}OOC(CH_2)_3CO-]_x$	5	27	77-80
Polyeicosamethylene adipate . . .	$[-O(CH_2)_{20}OOC(CH_2)_4CO-]_x$	6	28	85-87
Polyeicosamethylene pimelate . .	$[-O(CH_2)_{20}OOC(CH_2)_5CO-]_x$	7	29	82-84
Polyeicosamethylene suberate . .	$[-O(CH_2)_{20}OOC(CH_2)_6CO-]_x$	8	30	86-88
Polyeicosamethylene azelate . . .	$[-O(CH_2)_{20}OOC(CH_2)_7CO-]_x$	9	31	84-87
Polyeicosamethylene sebacate . .	$[-O(CH_2)_{20}OOC(CH_2)_8CO-]_x$	10	32	87-92

polyesters of sufficiently high molecular weight cannot be prepared from oxalic and malonic acids on account of the great tendencies of these acids to undergo thermal decomposition with evolution of carbon dioxide and formation of monocarboxylic acids [2]. The starting materials for the preparation of the other polyesters were 1,20-eicosanediol and the free dicarboxylic acids. The properties of the polyesters obtained are given in the table.

As will be seen from the results given in the table, the melting points of the polyesters obtained are dependent in a definite manner not only on the number of carbon atoms in the molecule of the acid, but also on whether this number is even or odd. Polyesters derived from dicarboxylic acids having even numbers of carbon atoms in their molecules have higher melting points than those derived from acids having odd numbers of carbon atoms, as will be particularly clear from Fig. 1, in which the relation between the melting point of the polyester of eicosanediol and the number of carbon atoms in the dicarboxylic acid molecule is represented graphically.

The dependence of the melting points of the polyesters on the number of carbon atoms in the acid is represented in Fig. 1 by a discontinuous curve, whereas the variation in the melting points of polyesters derived from acids having even numbers of carbon atoms is represented by a smooth curve (broken line in Fig. 1); another smooth curve (the second broken line in Fig. 1) represents the melting point variation for polyesters derived from

acids having odd numbers of carbon atoms. The difference in form of these broken lines is worthy of note: it is to be related, of course, to the difference in the effect of increasing the number of carbon atoms in the two series of polyesters, derived from dicarboxylic acids having even and odd numbers of carbon atoms respectively.

We shall therefore make separate examinations of the effect of increasing the number of carbon atoms in the original dicarboxylic acid on the properties of eicosanediol polyesters of the "even series", of the same effect for the "odd series", and finally of the effect of passing from odd to even and back. Examination of Fig. 1 permits us to conclude that an increase of two in the number of carbon atoms in passing to the succeeding acid in the series of acids having even numbers of carbon atoms has no appreciable effect on the melting points of the polyesters, the individual steps being between 1° and 3°, and the total change from oxalic to sebacic acid being only 3°. Much greater changes occur in the polyesters derived from the "odd" acids: the change in the melting point from malonic to glutaric acid is 10°, from glutaric to pimelic 4°, and from pimelic to azelaic 3°, the total change from malonic to azelaic being 17°. Still greater changes are observed when we examine the whole series of these polyesters and compare even and odd compounds. The great change occurring in melting point when we pass from polyesters of even acids to polyesters of odd acids will be obvious; the former melt at higher temperatures than the latter.

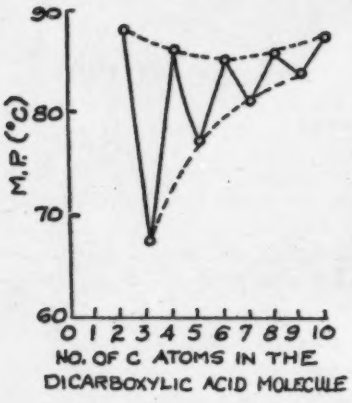

Fig. 1. Dependence of the melting points of eicosanediol polyesters on the number of carbon atoms in the acid component.

In order to determine the causes of the observed variations in the melting points of polyesters of eicosanediol, we must take into consideration the fact that polyethylene, which has a polymethylene chain, melts at 105°. All of the polyesters that we have prepared melt at lower temperatures, in spite of the low proportion of ester linkages in the molecule, which would lead us to expect a great similarity between these polyesters and polyethylene. This low melting point of the polyesters, in comparison with that of polyethylene, must evidently be associated with the increase in the flexibility of the polymer chain resulting from the introduction of oxygen linkages. Thus, polyethylene oxide [3] melts at 50-60°, and polydecamethylene oxide [4] at 58-60°. The increase in the flexibility of chains containing oxygen linkages is to be explained, as Aleksandrov and Lazurkin [5] have shown, in the following manner: the rotation of methylene groups around the bonds that unite them is not completely free owing to the resistance offered by the hydrogen atoms when they approach one another in the course of the rotation. The overcoming of this resistance requires an activation energy of 3000 cal/mole, whereas in the C—O—C linkage the activation energy is practically zero, there being no substituents on the oxygen to hinder free rotation around the C—O bond. For this reason the presence of C—O—C linkages in the chain increases its flexibility. These considerations are valid not only for polymers, but also for low-molecular-weight compounds, as can be seen from Fig. 2, in which curves are shown that indicate the changes in melting point in homologous series of alkanes, ethers, ketones, and carboxylic esters. Introduction of an ether linkage lowers the melting point, and the introduction of a carbonyl group raises it. Introduction of an ester linkage lowers the melting point, as can be seen from Fig. 2, in which the melting points in the homologous series of esters lie below those of the corresponding hydrocarbons. We may therefore conclude that, in the ester linkage C—O—CO—C, the effect of the ether linkage C—O—C predominates over that of the carbonyl group, resulting in the considerable lowering in melting point that we observe for the esters. As this relationship is valid for a large number of the members of homologous series of alkanes, ketones, ethers, and esters, it may clearly be extended to the class of polyesters, and in it we recognize the explanation of the results obtained in our investigation of the eicosanediol polyesters.

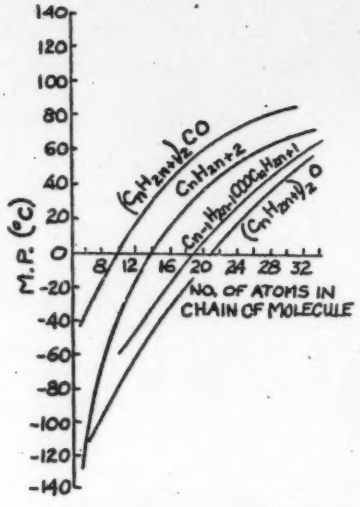

Fig. 2. Dependence of the melting points of ethers, esters, hydrocarbons, and ketones on the number of atoms in the chain of the molecule.

In the series of polyesters derived from acids having odd numbers of carbon atoms, the melting points rise as the number of methylene groups in the acid increases; this is readily explained by the reduction in the concentration of ester groupings and the increase in that of the methylene groups, for as ester groupings cause a fall in the melting point, and methylene groups a rise, it is understandable that the general effect will be a rise in melting point. These considerations, however, cannot be applied to the series of polyesters derived from even acids, since we do not find here such a considerable variation in melting point as the number of methylene groups in the chain of the original acid is increased.

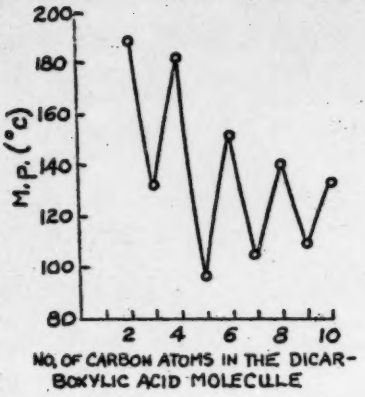

Fig. 3. Dependence of the melting point of a dicarboxylic acid on the number of carbon atoms in its molecule.

As we have already pointed out, comparison of polyesters derived from even and odd dicarboxylic acids reveals an obvious periodic variation in melting point: all polyesters derived from even acids melt higher than those derived from odd acids (see Fig. 1). If this behavior is compared with that of the dicarboxylic acids themselves, a considerable measure of resemblance between the courses of the curves will be noted (see Fig. 1 and Fig. 3).

As Nekrasov showed [6], the source of the periodic variation in the melting points and other physical properties in the homologous series of dicarboxylic acids lies in the differences in the configurations (cis-trans) of the even and odd dicarboxylic acids, which result, of course, in differences in the closeness of packing in the crystal and to differences in the strengths of the forces holding the molecules of dicarboxylic acid together in the crystal lattice; these, in their turn, find their expression in differences of melting point and other properties. Korshak and Rogozhin [2] have, for example, shown that the decarboxylation temperatures of dicarboxylic acids also vary in a periodic fashion, the odd dicarboxylic acids decomposing at lower temperatures than the even ones (see Fig.4).

The same factors, of course, preserve their significance also in the series of dicarboxylic acid polyesters, since they are determined by forces and causes of the same sort and order of magnitude. It may be considered that the main cause is the variation in the polarization of atoms in the acid molecule, which is determined by the variation in the distribution of charges. This must determine the closeness of packing and the strength of the forces binding the polyester macromolecules together – and therefore also the melting point, which is an expression of the strength of these forces.

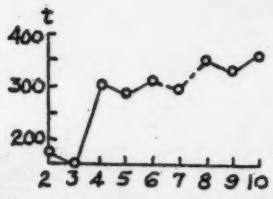

Fig. 4. Dependence of the dicarboxylation temperature of a dicarboxylic acid on the number of carbon atoms in its molecule.

EXPERIMENTAL

1,20-Eicosanediol

A 5% ethanolic solution of the diacetic acid of 1,20-eicosanediol, to which 5% on the weight of ester of hydrochloric acid had been added, was boiled under reflux for six hours in a round-bottomed flask. The reaction mixture was then transferred to a Favorsky flask, and ethyl acetate and excess of ethanol were distilled off. The residue was poured into a beaker and set aside overnight. The precipitate of eicosanediol was filtered off, washed several times with alcohol until the reaction to litmus was neutral, and air-dried. The eicosanediol was a white powder, melting at 101.5°; the literature gives m.p. 103° [7]. A 65-70% yield was obtained.

Polyeicosamethylene Sebacate

1,20-Eicosanediol (1.93 g) and sebacic acid (3 g) were placed in a condensation tube and heated in a bath of Wood's metal, constant temperature being maintained with the aid of a contact thermometer and a mercury relay. The reaction was at first carried out at 190° for 12 hours with continuous passage of nitrogen freed from oxygen; nitrogen was then excluded, and the system was connected to a vacuum pump, heating being continued at a pressure of 2-3 mm Hg at 210° for five hours. The temperature was then raised to 255°, and heating was continued under these conditions for a further 18 hours. The polyeicosamethylene sebacate was a white solid, readily dissolved when warmed with benzene, toluene, or xylene. When solutions in these solvents are cooled, the polymer

is precipitated: from benzene solution at 28.5°, from toluene solution at 36°, and from xylene solution at 29.5°. In this respect polyeicosamethylene sebacate is very similar to polyethylene, which dissolves hot, and precipitates when the solutions cool. Polyeicosamethylene sebacate is soluble in cresol in the cold. It melts at 87-92°. Its specific viscosity (0.5% solution in cresol) is 0.176.

With the exception of the polyesters derived from oxalic and malonic acids, the remaining polyesters were prepared by the same method. The polyesters of oxalic and malonic acids were prepared by heating 1,20-eicosanediol with the ethyl or isopropyl esters of these acids taken in 150% excess. The properties of all of the polyesters are given in the table.

SUMMARY

1. A study has been made of the polycondensation of 1,20-eicosanediol with succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids and with esters of oxalic and malonic acids.

2. The polyesters formed by 1,20-eicosanediol with oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids have been prepared.

3. A discussion has been given of the causes of the differences observed in the melting points of the synthesized polyesters of 1,20-eicosanediol with dicarboxylic acids.

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BRIEF COMMUNICATIONS

CERTAIN DERIVATIVES OF AMINOMETHYLPHOSPHONIC ACID

M. I. Kabachnik and T. Ya. Medved

Aminomethylphosphonic acid, a phosphorus analog of glycine, has received very little study. Only a few methods for its preparation may be found in the literature [1, 2], and the best of these is the method that we have developed: the ammonolysis of diethyl chloromethylphosphonate [3]. We have described also the alkylation of aminomethylphosphonic acid with dimethyl sulfate, which resulted in the formation of the "phosphonobetaine" $(CH_3)_3\overset{+}{N}CH_2PO(OH)O^-$.

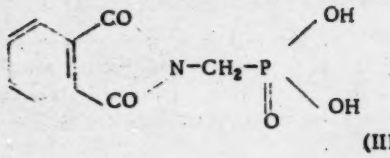
With the object of investigating the properties of aminomethylphosphonic acid and comparing them with those of glycine, we have carried out some acylation and alkylation reactions. It was found that aminomethylphosphonic acid is more difficult to acylate than glycine. Acetylation can be effected by heating aminophosphonic acid with excess of acetic anhydride in a water bath, when acetamidomethylphosphonic acid (I) is obtained in 57% yield.

$CH_3CONHCH_2PO(OH)_2$ (I)

$ClCH_2CONHCH_2PO(OH)_2$ (II)

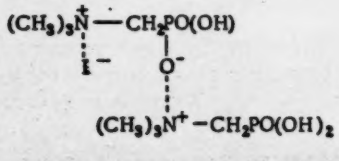
Fischer's method for the chloroacetylation of glycine in aqueous alkaline medium with chloroacetyl chloride [5] was found to be applicable to aminomethylphosphonic acid, but the yield was not good: (chloroacetamido)methylphosphonic acid (II), which was isolated as the aniline salt, was formed in 32% yield.

Fusion of aminomethylphosphonic acid with phthalic anhydride resulted in a 33% yield of the corresponding phthalimide derivative (III).

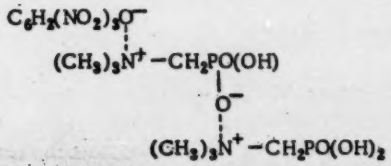


(III)

Interesting results were obtained when aminomethylphosphonic acid was alkylated with methyl iodide. When these substances were heated together in a sealed tube at 200-220°, unchanged aminomethylphosphonic acid was recovered from the reaction mixture. When, however, the reaction was carried out under the same conditions, but in a medium of methanol, an excellent yield was obtained of a quaternary iodide (IV) derived from the phosphonobetaine and containing two molecules of phosphonobetaine per iodide ion.



(IV)



(V)

This iodide behaved as a tribasic acid when titrated with caustic soda in presence of phenolphthalein. When treated with moist silver oxide, it was quantitatively converted into the phosphonobetaine, m.p. 267°. An iodide of the same composition can be prepared from the free phosphonobetaine by the action of concentrated hydriodic acid, even when the latter is taken in great excess. It is evidently a general property of the phosphonobetaine to form salts of similar composition; thus we have previously [4] described a picrate of the phosphonobetaine that contained one molecule of picric acid for every two molecules of the phosphonobetaine (V).

In the methylation of aminomethylphosphonic acid with methyl iodide and methanol, a very small amount of methyl iodide is required: when reaction occurs in methanol at 200-220°, only 20% of the theoretically required amount of methyl iodide is sufficient to enable a 62% yield of the quaternary iodide to be obtained. This behavior must doubtless be attributed to re-formation, under the conditions of the reaction, of methyl iodide by reaction of methanol with hydriodic acid liberated during the methylation of the amino group. The methylation is brought about, in effect, by methanol, but in absence of methyl iodide it does not, of course proceed.

EXPERIMENTAL

Acetamidomethylphosphonic Acid

A mixture of 0.9 g of aminomethylphosphonic acid and 8 ml of acetic anhydride was heated in a boiling water bath for 2 hours 30 minutes. Excess of acetic anhydride was distilled off under reduced pressure, and the undistillable residue was treated with hot methanol. The solution obtained was concentrated, and when it had cooled down slightly yellowish crystals separated; they were recrystallized from methanol, yielding 0.7 g (57%) of product, m.p. 185°.

	Found %:	C 24.19; 24.05;	H 5.19; 4.95;	N 9.48; 9.57;	P 20.26; 20.32
$C_3H_8NPO_4$	Calculated %:	C 23.53	H 5.23	N 9.15	P 20.26

The substance titrated as a dibasic acid (against caustic soda with phenolphthalein as indicator). Equivalent weight: found 80.8, calculated 76.5.

(Chloroacetamido)methylphosphonic Acid

Aminomethylphosphonic acid (2.2 g) was dissolved in 19.7 ml of 2 N NaOH. The cooled solution was stirred, and chloroacetyl chloride (4.4 g) and 2 N NaOH (22.4 ml) were added alternately in small portions. An addition was then made of 6 ml of 5 N hydrochloric acid, and the liquid was evaporated down under reduced pressure at 30-35°. The residue, which was a white crystalline mass, was extracted several times with ethanol, and an alcoholic solution of aniline was added to the extract. The 1.2 g of white crystalline material that separated melted at 157°. The salt could be recrystallized from ethanol, but this treatment did not affect the melting point.

	Found %:	C 37.81; 38.42;	H 5.17; 5.20;	N 9.84; 10.17;	P 11.44; 11.46
		Cl 12.50; 12.46			
$C_3H_7NO_4Cl \cdot C_6H_5NH_2$	Calculated %:	C 38.50;	H 4.99;	N 9.98;	P 11.05; Cl 12.66

Phthalimidomethylphosphonic Acid

A mixture of 1.1 g of aminomethylphosphonic acid and 1.5 g of phthalic anhydride was melted by being heated gently over a gauze. The cooled melt was treated with hot ethanol, and the undissolved crystals of unchanged aminomethylphosphonic acid were filtered off. The filtrate, after evaporation, yielded 0.8 g (33%) of a colorless crystalline substance, which melted over the range 280-285°.

	Found %:	C 45.12; 45.15;	H 3.08; 2.74;	H 5.50; 5.33;	P 12.78; 12.95
$C_9H_8NPO_5$	Calculated %:	C 44.80	H 3.30	N 5.80;	P 12.86

Attempt to Methylate Aminomethylphosphonic Acid with Methyl Iodide

A mixture of 1 g of aminomethylphosphonic acid and 3 ml of methyl iodide was heated in a sealed tube at 200-220° for six hours. The aminomethylphosphonic acid was recovered unchanged from the reaction mixture.

Methylation of Aminomethylphosphonic Acid with Methyl Iodide in Methanol

A mixture of 2 g of aminomethylphosphonic acid, 6 ml of methyl iodide, and 6 ml of methanol was heated in sealed tubes at 200-220° for six hours (to prevent the tubes from breaking, they were placed in an autoclave in which a pressure of about 40 atm was established). When the tubes were opened, evidence of considerable pressure was noted. Methyl iodide was evaporated off, and the crystals that remained behind were recrystallized from methanol, yielding 3.2 g (82%) of a colorless crystalline substance, m.p. 220°.

Found %: C 21.90; 22.07; H 5.67; 5.55; N 6.45; 6.70; P 14.35; 14.40; I 29.47; 29.34

$C_8H_{22}N_2P_2O_6I$. Calculated %: C 22.12; H 5.76; N 6.45; P 14.30; I 29.26

Equivalent by iodine: found 435, calculated 434. Equivalent acidimetrically: found 145.8, calculated for a tribasic acid 144.7.

Methylation of Aminomethylphosphonic Acid with Insufficient Methyl Iodide in a Medium of Methanol

A mixture of 1 g of aminomethylphosphonic acid, 0.4 ml of methyl iodide (20% of the theoretically required amount), and 5 ml of methanol was heated in a sealed glass tube for six hours at 200-220°. The tube was opened, and the liquid was distilled, leaving 1.2 g (62%) of the iodide derived from the "phosphonobetaine" as residue.

The "Phosphonobetaine"

An aqueous solution of 2.7 g of the quaternary iodide of m.p. 220° was shaken with excess of freshly prepared moist silver oxide. Silver iodide and excess of silver oxide were filtered off, and the solution was treated with hydrogen sulfide. Precipitated silver sulfide was filtered off, and the filtrate was evaporated until a residue of constant weight was obtained. This was then recrystallized from absolute ethanol, yielding 1.35 g (87.0%) of the phosphonobetaine, m.p. 267°. A mixed melting point of this substance and the phosphonobetaine synthesized previously from aminomethylphosphonic acid and dimethyl sulfate showed no depression.

Found %: P 20.48; 20.38

$C_4H_{12}NPO_3$. Calculated %: P 20.26

Preparation of the Iodide Derived from the Phosphonobetaine from the Betaine and Excess of Hydriodic Acid

The phosphonobetaine (1 g) was dissolved in a small amount of water, and concentrated hydriodic acid (30 ml) was added to the resulting solution. The solution was evaporated down in a dish on a water bath, and the residue was dissolved in a small amount of water and reprecipitated with absolute ethanol, yielding 0.8 g of the iodide derived from the phosphonobetaine, m.p. 215°.

SUMMARY

1. Experiments on the acylation of aminomethylphosphonic acid show that it proceeds with greater difficulty than the acylation of glycine. Acetamidomethyl-, (chloroacetamido)methyl-, and phthalimidomethyl-phosphonic acids have been prepared.

2. The methylation of aminomethylphosphonic acid has been effected by means of methyl iodide in a methanol medium, and it has been shown that a quaternary iodide derived from the phosphonobetaine is formed. It has been established that methylation proceeds at the expense of methanol, so that much less than the stoichiometric amount of methyl iodide may be used.

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SYNTHESIS OF 1-BUTENE-4-C^{14} AND BUTANE-1-C^{14}

M. B. Neiman and G. I. Feklisov

The most widely used method for the introduction of radioactive carbon into the molecule of a hydrocarbon is the carbonation of alkylmagnesium halide complexes with radioactive carbon dioxide $C^{14}O_2$ [1]. 1-Butene-4-C^{14} and butane-1-C^{14} may, therefore, be synthesized according to the following schemes:

$$C_3H_7I \xrightarrow{Mg} C_3H_7MgI \xrightarrow{C^{14}O_2} C_3H_7C^{14}OOMgI \xrightarrow{H_2O} C_3H_7C^{14}OOH \xrightarrow{C_4H_9OH} C_3H_7C^{14}OOC_4H_9 \xrightarrow[250°;\ 400\ atm]{Cu\text{-}Cr} \longrightarrow C_3H_7C^{14}H_2OH. \quad (1)$$

$$C_3H_7C^{14}H_2OH \xrightarrow{(HI)} C_3H_7C^{14}H_2I \xrightarrow{Mg} C_3H_7C^{14}H_2MgI \xrightarrow{H_2O} C_3H_7C^{14}H_3$$
$$C_3H_7C^{14}H_2OH \xrightarrow{(Al_2O_3)} C_2H_5CH{=}C^{14}H_2 \xrightarrow[Ni]{H_2} CH_3CH_2CH_2C^{14}H_3. \quad (2)$$

The synthesis of compounds labeled with radiocarbon by reactions similar to those in the first scheme has been carried out by Andreev and Andrianova [2].

In our laboratory we have prepared the labeled hydrocarbons propene-2-C^{14} [3], pentane-1-C^{14}, and pentane-3-C^{14} [4], and here we again used the method of carbonizing alkylmagnesium halide complexes with radioactive carbon dioxide. This method of preparing labeled hydrocarbons suffers, however, from a number of defects, e.g., the low yield of product and the large number of laborious operations.

The difficulties can be considerably lightened by the use of lithium aluminum hydride in the synthesis. A brief note has been published regarding a rational scheme for the preparation of 1-butene-4-C^{14} and butane-1-C^{14} [5]. The detailed working out of the synthesis of 1-butene-4-C^{14} and butane-1-C^{14} was performed by us with nonradioactive materials. The compounds were prepared in accordance with the following schemes:

$$BaC^{14}O_3 \xrightarrow{H_2SO_4} C^{14}O_2 \xrightarrow{LiAlH_4} C^{14}H_3OH \xrightarrow{PI_3} C^{14}H_3I \xrightarrow{Mg} C^{14}H_3MgI \xrightarrow{CH_2=CH-CH_2Br} C^{14}H_3CH_2CH{=}CH_2. \quad (3)$$

$$C^{14}H_3CH_2CH{=}CH_2 \xrightarrow[Ni]{H_2} C^{14}H_3CH_2CH_2CH_3. \quad (4)$$

Synthesis of 1-Butene-4-C^{14}. This was based on labeled methyl iodide prepared by the method that we have previously described [6]. Methylmagnesium iodide was prepared from 32 g of methyl iodide by reaction with magnesium in 50 ml of dibutyl ether, which had been previously dried over sodium and redistilled on a sand bath. The synthesis of butene was carried out in the apparatus shown diagrammatically in Fig. 1. The solution of methylmagnesium iodide in dibutyl ether was poured through a glass filter (to remove unchanged magnesium) into the reaction flask 1, which was heated in the water bath 6 to 70°. At this temperature, allyl bromide (30 g) was added dropwise from the funnel 2. The reaction of allyl bromide with methyl-C^{14}-magnesium iodide yielded 1-butene-4-C^{14} [7], which was collected in the trap 5, which was cooled with liquid nitrogen.

The 1-butene-4-C^{14} was purified by fractionation through a highly efficient low-temperature column. From 32 g of labeled methyl iodide, 7 g (55%) of 1-butene-4-C^{14} was obtained. In order to check the purity of the butene obtained, its vapor pressure was determined at a number of temperatures: the experimental points (Fig. 2) fall close to the vapor pressure curve for 1-butene, as constructed from data in the literature [8]. The butene obtained was subjected to combustion at 500° over copper oxide, and the carbon dioxide formed was converted into barium carbonate by treatment with baryta water. The radioactivity of the barium carbonate was determined with a surface counter, and the results are given in the table.

Synthesis of Labeled Butane. This was performed by the reduction of 1-butene-4-C^{14} with gaseous hydrogen over pyrophoric nickel. Into the autoclave 1 (Fig. 3) we placed 2 g of an alcoholic suspension of pyrophoric nickel and a sealed glass tube 3 which contained 5 g of 1-butene-4-C^{14} and had been cooled in liquid nitrogen. The air was pumped

out of the autoclave, the valve was closed, and the electric furnace 2 was switched on so as to heat the tube of butene contained in the autoclave.

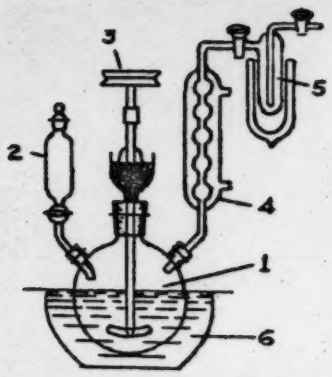

Fig. 1. Diagram of the apparatus for the synthesis of 1-butene-4-C^{14}: 1 – reaction flask; 2 – dropping funnel; 3 – stirrer; 4 – condenser; 5 – trap; 6 – water bath

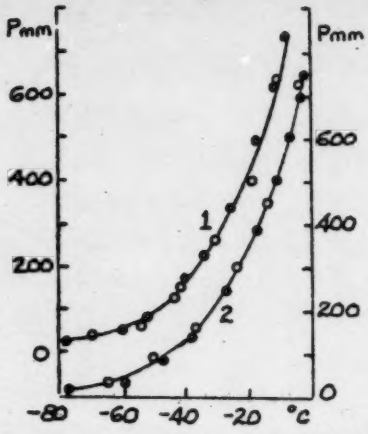

Fig. 2. Vapor pressure curves for butene (1) and butane (2). o – data from literature; o – experimental results (scale for butene on left; scale for butane on right)

At 80° the tube broke: the occurrence of this event was indicated by the reading of the manometer 4. In this was the autoclave was filled with butene. It was now cooled to room temperature and hydrogen was passed in from a cylinder until a pressure of 115 atm was attained. Agitation of the contents of the autoclave was effected by rotation of the latter by means of the electric motor 6. Hydrogenation of the butene proceeded to an extent of 85% in the first 30 minutes. When hydrogenation was complete, the butane formed was drawn from the autoclave with a pump and frozen with liquid nitrogen in the traps (8).

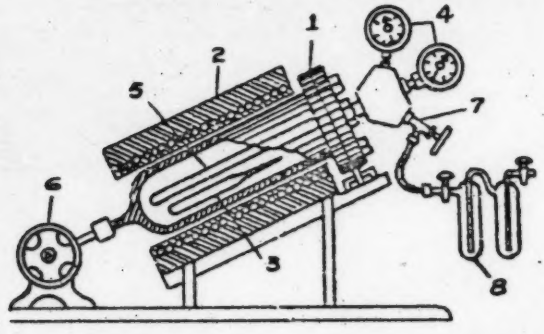

Fig. 3. Diagram of apparatus for the hydrogenation of butene to butane: 1 – autoclave; 2 – electric furnace; 3 – tube of butene; 4 – manometer; 5 – thermocouple; 6 – electric motor; 7 – valve; 8 – trap

The butane was purified by passage through wash bottles of bromine water and of concentrated sulfuric acid, and was then fractionated through a highly efficient column. From 5 g of 1-butene-4-C^{14}, 4.9 g of butane-1-C^{14} was obtained, the yield being, therefore, about 95%. The purity of the product was checked by determining its vapor pressure at various temperatures, and the results fitted satisfactorily to the curve constructed for butane from data in the literature [9]. By combustion of the butane-1-C^{14} and absorption of the $C^{14}O_2$ obtained in baryta water, the C^{14} present was converted into barium carbonate.

The results of the determinations of the specific activity of the butane-1-C^{14} obtained are given in the table. It will be seen from the table that the specific activities of both the butane-1-C^{14} and the 1-butene-4-C^{14} were practically identical with that of the starting material, $C^{14}H_3I$. Our comparisons of the activities of the three substances were, of course, based on figures relating to one active carbon atom.

TABLE

Relative Radioactivities of Synthesized 1-Butene-4-C^{14} and Butane-1-C^{14}

Compound	Weight of $BaC^{14}O_3$ precipitate (mg)	Calculated activity (imp./min)	Specific activity of $BaC^{14}O_3$ (imp·cm²/min·mg)	Specific activity of $BaC^{14}O_3$ per C atom
$C^{14}H_3I$	10.5	4346 ± 250	1500	1500
	11.7	4438 ± 250	1500	1500
$C^{14}H_3CH_2CH=CH_2$	23.8	1283 ± 70	370	1480
	20.8	1253 ± 70	370	1480
$C^{14}H_3CH_2CH_2CH_3$	15.6	1196 ± 70	370	1480
	17.4	1265 ± 70	370	1480
	15.6	1249 ± 70	370	1480

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TABLE OF CONTENTS (continued)

	Page	Russ. page
19. Synthesis of Steroid Compounds and Related Substances. Communication XXIII. Synthesis of Sulfur Analogs of Steroids by Diene Condensation of Cyclic γ-Keto Sulfones with Bicyclic Dienes. I. N. Nazarov, I. A. Gurvich, and A. I. Kuznetsova	969	1091
20. Synthesis of Polycyclic Compounds Related to Steroids. Communication XXV. Synthesis of Compounds Related to Estrone by the Diene-condensation Method. I. N. Nazarov and I. L. Kotlyarevsky	977	1100
21. Stability of Skeletal Nickel Catalyst at Elevated Temperature. L. Kh. Freidlin and K. G. Rudneva	987	1111
22. Macromolecular Compounds. Communication 60. Role of Stereochemical Factors in the Polymerization Process. V. V. Korshak and N. G. Matveeva	991	1116
23. Macromolecular Compounds. Communication 63. Polyesters of 1,20-Eicosanediol. V. V. Korshak and S. V. Vinogradova	995	1121
Brief Communications		
24. Certain Derivatives of Aminomethylphosphonic Acid. M. I. Kabachnik and T. Ya. Medved	999	1126
25. Synthesis of 1-Butene-4-C^{14} and Butane-1-C^{14}. M. B. Neiman and G. I. Feklisov	1003	1129

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